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ART. LII.—*Electro-Chemical Effects due to Magnetization;* by GEORGE OWEN SQUIER, Ph.D., Lieut. U. S. Army.

Introduction.

THE influence of magnetism on chemical action was the subject of experiment by numerous investigators during the first half of the present century.* Up to 1847, we find, by no means, a uniformity of statement in regard to this subject, and secondary effects were often interpreted as a true chemical influence. Among the earlier writers who maintained that such an influence exists, may be mentioned Ritter, Schweigger, Döbreiner, Fresnel, and Ampère, while those of opposite view were Wartmann, Otto-Linné Erdmann, Berzelius, Robert Hunt and the Chevalier Nobili.

Professor Remsen's discovery in 1881, of the remarkable influence of magnetism on the deposition of copper from one of its solutions on an iron plate, again attracted attention to the subject, and since then considerable work has been done directly or indirectly bearing on the question.

Among other experiments by Professor Remsen† were the action in the magnetic field of copper on zinc, silver on zinc, copper on tin, and silver on iron, in all of which cases the magnet evidently exerted some influence. With copper sulphate on an iron plate the effects were best exhibited, the copper being deposited in lines approximating to the equipotential lines of the magnet, and the outlines of the pole being distinctly marked by the absence of deposit.

* Wartmann, Philosophical Magazine, III, xxx, p. 264, 1847.

† American Chem. Jour., vol. iii, 157, vol. vi, 430. Science, vol. i, No. 2, 1883.

Messrs. Nichols and Franklin* were the next to conduct experiments bearing on this subject. They found that finely divided iron, which has become "passive" through the action of strong nitric acid, suddenly regains its activity when introduced in a magnetic field, and also that when one of the two electrodes immersed in any liquid capable of chemically acting upon them, is placed in a magnetic field, a new difference of potential is developed between them due to this magnetization. They ascribe these effects to electric currents in the liquid produced indirectly by the magnet, which currents go in the liquid from the magnetized to the neutral electrode.

Professor Rowland and Dr. Louis Bell† were the first to note the "protective action" of points and ends of magnetic electrodes, and to give the exact mathematical theory of this action. Their results were *directly opposite* to those of Messrs. Nichols and Franklin, who found, as stated above, that points and ends of bars in a magnetic field acted like zincs to the other portions, or were more easily dissolved by the liquid.

The method of experiment adopted by Professor Rowland was to expose portions of bars of the magnetic metals placed in a magnetic field to reagents which would act upon them chemically, and study the changes in the electro-chemical nature of the exposed parts by fluctuations in a delicate galvanometer connected with the two bars. Iron, nickel, and cobalt were experimented upon and nearly thirty reagents were examined in this manner. The results are summed up in the following statement: "When the magnetic metals are exposed to chemical action in a magnetic field, such action is decreased or arrested at any points where the rate of variation of the square of the magnetic force tends towards a maximum."

Other investigations in this field are those of Andrews,‡ who employed iron and steel bars from eight to ten inches long with their ends immersed in various solutions, and one bar magnetized by means of a solenoid. The protective action was not noted, but, on the contrary, the magnetized bars acted as zincs to the neutral bars, thus indicating that they were more easily attacked.

Practically the same results were obtained by Dr. Theodor Gross;§ soft iron wires 8^{cm} long, and 3^{cm} in diameter coated with sealing wax, except at the ends, were exposed to various

* This Journal, xxxi, 272, xxxiv, 419, xxxv, 290.

† Philosophical Magazine, xxvi, 105.

‡ Proceedings of the Royal Society, No. 44, pp. 152–168, and No. 46, pp. 176–193.

§ Ueber eine neue Entstehungsweise galvanischer Ströme durch Magnetismus. —Sitzungsberichte der Wiener Akademie, 1885, vol. xcii, '85, p. 1373.

liquids. When one electrode was magnetized a current was obtained going in the liquid from the magnetized electrode to the non-magnetized electrode.

It thus appears that there is at least an apparent inconsistency between the protective results of Professor Rowland and Professor Remsen, and those of Nichols, Andrews, Gross and others, who find the more strongly magnetized parts of iron electrodes more easily attacked than the neutral parts, and it was with the object of endeavoring to reconcile these results, and of studying the *exact nature* of the influence exerted by the magnet, that the experiments recorded in this paper were undertaken.

Apparatus and Method of Investigation.

The method of investigation was that adopted by Professor Rowland in his previous work on the subject, since its facility and delicacy permitted the effects of the magnet to be observed whenever there was the slightest action on the electrodes by the solution examined, and the investigation could thus be carried over a wide range of material.

A large electromagnet was employed to furnish the magnetic field, and, at a distance sufficient to prevent any direct influence due to the magnet, a delicate galvanometer of the Rowland type was set up. Small cells were made of iron electrodes of special forms, coated with sealing wax, except at certain parts, and immersed in a liquid capable of acting chemically on iron. The whole was contained in a 50^{cc} glass beaker, and when joined to the connecting wires of the distant galvanometer was firmly clamped between the poles of the electromagnet.

In the course of the examination of a number of substances it was found necessary to use two galvanometers, one specially made by the University instrument maker and very sensitive, which was employed with acids which evolve hydrogen, the other much less sensitive was best suited to the violent "throws" with nitric acid and iron. The samples of iron used throughout the experiments were obtained from Carnegie, Phipps & Co. of Pittsburg, and were practically pure.

In order to insure a uniform density of surface, the electrodes were turned from the same piece and polished equally with fine emery cloth. The magnet could be made or reversed at the galvanometer, and its strength varied at will by a non-inductive resistance. The electro-chemical effects due to the magnetic field could thus be studied with facility by the fluctuations of the galvanometer needle. The original difference of potential which always existed between the electrodes was compensated by a fraction of a Daniell cell, so the

effects of a variation of the magnetic field could be observed when no original current was passing between the electrodes.

The standard cells were made with care, and under uniform treatment possessed at 20° C. an electromotive force of 1·105 volts. The connections with the compensating circuit, which contained a finely divided bridge, were so arranged that from its readings the difference of potential between the distant electrodes became known at once without involving the resistance of the cell or of the galvanometer.

Since quantitative measurements of the effects observed were desired, a preliminary step was to calibrate the electromagnet for a given distance apart of the pole-pieces. The method employed was the well-known one of comparing the galvanometer deflections produced by a test-coil in the field with those of an Earth Inductor in series in the circuit. Since the effect of the sudden addition of a certain strength of field was wanted instead of its absolute value, the deflections with the test-coil were taken for simple "make" or "break" and not for reversed field, thus eliminating the residual magnetism of the pole-pieces.

In the formula applicable, viz: $\frac{H}{H'}\frac{\pi n a^2}{\pi n' a'^2} = \frac{d}{d'}$ nearly, in which d and d' represent the deflections due to the Inductor and test-coil respectively; H and H′ the earth's field and the field to be measured; n and n' the number of turns and a and a' the radii of the coils, the particular values were

$$\pi n a^2 = 20716^{\text{sq cm}}$$
$$\pi n' a'^2 = 6{\cdot}788^{\text{sq cm}}$$
$$d = 4{\cdot}697$$

Distance between pole-pieces $3{\cdot}5^{\text{cm}}$.

$H' = 1299{\cdot}48\, d'H$, and as d' varied from $\frac{1}{20}$ to 16, the range of field employed was from 65 to 20,800 H.

A curve was constructed so that from accurate ammeter readings in the field circuit, the strength in absolute measure could be read off at once.

Experimental Results.

Preliminary.—The first experiments were made with very dilute nitric acid and iron electrodes, one a circular disc of 5^{mm} radius, and the other a small wire 1^{cm} long and 1^{mm} in diameter turned to a sharp point at one end. The point was placed opposite the center of the disc, at a distance of 1^{cm} from it, and the whole placed so that the cylindrical electrode coincided with the direction of the lines of force. When the minute point and the center of the disc were exposed to the

liquid, and the magnet excited, a momentary "throw" of the galvanometer was observed in the direction indicating the point as being protected or acting as the copper of the cell.

When the pointed pole was slightly flattened at the end, and the insulation so cut away that the surfaces of exposure on the two electrodes were exactly the same, the throw of the galvanometer on making the field was very much diminished, although still perceptible, since the disposition of lines of force would still be very different over the two plane surfaces of exposure.

With ball and point electrodes precisely similar phenomena were observed as with a disc and point, except to a less degree.

The gradual reversal of the current shortly after exciting the field; the independence of the throw of the direction of the current through the magnet; the disappearance of the throw when the nature of the magnetic field at the exposed parts became the same; and the effects of artificially stirring the liquid were observed exactly as described by Messrs. Rowland and Bell.

In the course of a large number of preliminary experiments with nitric acid, it was soon observed that under certain conditions the effect of suddenly putting on the magnetic field, was to produce a less rapid deflection of the galvanometer in the *opposite* direction, or indicating the point as acting as a zinc. Plainly this irregular behavior, due to the magnet, required a more systematic study than it had yet received. It had been found that the reversal of the current which regularly followed the "protective throw" was decreased or destroyed by anything which prevented free circulation in the liquid, and that an acidulated gelatine, which was allowed to harden around the poles, was best suited for this purpose. The great irregularity observed in any one experiment made it necessary to eliminate everything possible which might mask the true phenomenon, if any accurate comparisons were to be drawn between the effects observed in the different cases, accordingly a standard form of experiment was adopted which was carefully repeated many times. The cell found best suited for this purpose was composed as follows:

Disc electrode, diameter	14·4 mm
thickness	2·6 mm
Point electrode, total length	15·2 mm
diameter	4·4 mm
length of point	5·2 mm
Distance of point from center of dise	10· mm

The same electrodes were used throughout any set of experiments, being carefully cleaned and polished each time.

With nitric acid the liquid was finally made up, as follows:

Distilled water	10 grams
Hard gelatine	1 gram
C. P. nitric acid (sp. gravity, 1·415),	0·533 grams

The gelatine and water were allowed to stand until the former had dissolved without the application of heat, when the acid was added, and the whole thoroughly mixed. Too strongly acidulated gelatine would not harden at all.

In some cases, in order to protect the point from the *beginning*, the electrodes, secured as usual at the ends of two small glass tubes containing the connecting wires, were firmly clamped in the proper position between the poles of the magnet, and the magnetic field put on before the cell was completed by pushing the beaker containing the solution up in position around the electrodes.

With this cell a series of parallel experiments were conducted to obtain the variation of the effects with time, or the amount of iron salts present; the fluidity of the solution, and with constant and variable magnetic fields.

A. Behavior of the cell with time, in the Earth's field.

The cell was placed entirely outside the magnetic field, and galvanometer readings taken at intervals of one minute for three hours. The curve fig. 1 (I) shows these results. Positive ordinates indicate a current from the point to the disc, and negative ordinates the reverse current. Other experiments with fresh solutions, same electrodes, same exposed area, and every condition as nearly as possible the same, gave curves of practically the same character, and the one given is selected to illustrate.

The curve indicates that the original current was to the point electrode, this gradually decreased due to polarization until after an hour and five minutes it reversed slightly, but again reversed thirty-five minutes later, and after a little more than two hours the deflection became perfectly constant, remaining so indefinitely.

The iron salts formed could not move with facility from the exposed surfaces through the hardened gelatine, and were easily outlined from their brown color, as the whole apparatus was placed in a strong light.

B. In a uniform magnetic field.

The cell was next placed in the magnetic field which was kept practically uniform (about 15,650 H) for three hours, and galvanometer readings taken as before.

The electrodes were magnetized before being introduced into the solution, so as to protect the point from the beginning. In order to prevent the influence of the rise of temperature due to the heating of the field coils of the electromagnet, the whole cell was packed with cotton wool between the poles. As Gross and Andrews observed the temperature effect was small, the solution rising but 0·7° C. in half an hour.

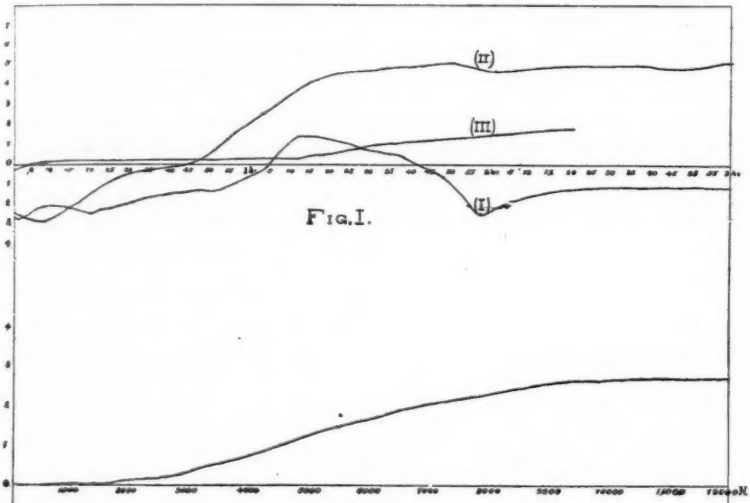

FIG. I.

FIG. 2.

FIG. 3.

The curve fig. 1 (II) shows the result of these observations. It is seen that the original current was as before to the point electrode, and about the same in value. This reversed after forty-five minutes, and rapidly increased to approximately twice its original value at the end of one hour and twenty

minutes, and instead of again reversing, remained indefinitely with the point electrode as a zinc. The distribution of the iron salts in this case was quite unlike the former. Notwithstanding the gelatine, the powerful magnetization of the exposed point gradually drew the iron salts from the disc as fast as they were formed, and concentrated them symmetrically about the point, giving the solution in this region an almost black appearance.

After waiting a sufficient time to be assured that further presence of iron salts would not effect the permanency of the existing electromotive force, the magnetic field was gradually decreased *without ever breaking circuit*, by increasing the liquid resistance in the field current. This change of resistance was necessarily made more or less suddenly, and the deflection experienced at each increase of resistance, a not very sudden throw toward reversal, in every respect the same as had been repeatedly observed in the preliminary experiments, and very different from the characteristic "protective throw" which is always sudden and in one direction.

By simply varying the field current with care, as explained above, the deflection could be reversed again and again at will, and could also be held at the zero of the scale indicating no current at all, as long as desired. When once the field was entirely broken the iron salts were released from the control of the exposed pole, seriously disturbed by gravity, and putting on the field again failed to reproduce the results noted above.

The only elements of difference in the two cases are, (*a*) the magnetized condition of the metal, (*b*) the distribution of the iron salts formed by the reaction.

Although, as the curves indicate, the average electromotive force with the magnetic field was much greater than in the former case, yet this electromotive force is due to the difference of action at the two exposed surfaces, and, as will be pointed out later, the total amount of iron dissolved and passing into solution in the two cases is probably not very different.* Quantitative experiments are wanting on this point.

The influence of the magnetized condition of the metal and its magnitude is exhibited in the phenomenon of the "protective throw" which is always observed with apparatus sufficiently delicate and unless it is masked by other secondary phenomena.

Since the electrodes were embedded in hardened gelatine, there could be no convection currents in the liquid and this can be eliminated. Evidently the great difference in the

* Fossati, Bolletino dell' Elettricista, 1890.

behavior of the cell in the two experiments described is principally due, either directly or indirectly, to the distribution of the iron salts formed by the reaction in the two cases.

The principal *time* effects of the magnet were:

(*a*) To produce a higher potential at the point of greater magnetization.

(*b*) To increase the rate of change of the potential between the electrodes and the absolute value of this potential difference.

(*c*) It also appears from both curves that after a certain distribution of iron salts is reached, further presence of the same does not effect the permanency of the current established.

Since the time effects of the magnet were so marked, it was thought possible that a "cumulative" effect, due to the Earth's field alone might be detected after a sufficient time had elapsed. The apparatus was made as delicate as possible, and parallel experiments conducted, the electrodes first being placed in the magnetic meridian, and afterwards perpendicular thereto. No positive difference could be detected.

C. Convection currents in the liquid.

As has already been stated, the reversal of the current which regularly followed the "protective throw" was found by Messrs. Rowland and Bell to wholly disappear when hardened acidulated gelatine was substituted for the dilute acid solution, so that when the magnet was put on, a permanent deflection of much less magnitude was obtained instead of a transitory throw. This indicated that currents in the liquid cannot be neglected, and their study was next undertaken. Since hardened gelatine completely prevented the reversal of the current, and with no gelatine it regularly appeared after a short time, a large number of experiments were made, in which the amount of gelatine was varied continuously between these limits. As expected the effects also varied, the greater the fluidity of the solution, the more quickly the reversal occurred.

In the light of what was already known concerning the presence of iron salts, some of the experiments were continued over a considerable time, and in others iron salts were introduced artificially, to increase the effects. It was soon found that by starting with a fresh hardened gelatine, with which the "protective throw" was the only feature, and gradually increasing the fluidity of the solution and the amount of iron salts present, both effects were exhibited at the making of the field, first, the sudden throw of the needle always in the direction to protect the point, and immediately thereafter the comparatively slow "concentration throw" in the opposite direc-

tion. By making the conditions still more unfavorable for the "protective throw," it gradually diminished until entirely masked by the second effect, so that making the field produced a deflection in the direction indicating a current from the point.

With the proper conditions both of these effects could be studied with the greatest ease: first, one made prominent, then both equal, then the other made prominent at will. The "protective throw" could be traced until it became a mere stationary tremor of the needle at the instant of its starting on the "concentration throw." This latter, though called a "throw," can be made to vary from an extremely slow continuous movement of the galvanometer deflection, as in experiment *B*, already described, to a comparatively rapid deflection at the instant of making the magnet.

By using simply a dilute nitric acid solution with no gelatine, and inserting a thick piece of glass between the electrodes, the concentration effect was delayed enough to allow the "protective throw" to first appear, with considerable iron salts in the solution, and on making the field both effects were observed as described above.

It now appears that the reversal of the current uniformly observed in the experiments of Messrs. Rowland and Bell was but a form of the "concentration throw" mentioned above, and that we can regard the substitution of the hardened acidulated gelatine for the dilute acid, as merely separating these effects, so that the former can be studied by itself; in other words, the reversal of the current would have occurred just the same after a sufficient time had elapsed.

Turning to the experiments of Drs. Gross and Andrews, they employed but one magnetized electrode which was not pointed. In this case the nature of the magnetic field at the two exposed surfaces would be very much more nearly the same than when a pointed electrode is employed. This arrangement is not therefore suited to bring out the delicate "protective throw," and it is not surprising that the concentration effect was the prominent feature observed.

We have now a complete reconciliation of the *directly opposite results* referred to in the introduction. The "protective throw" is due to the actual attraction of the magnet for the iron, and is always in the direction to protect the more strongly magnetized parts, while the "concentration throw" is always in the opposite direction, and depends upon the distribution of the iron salts present in the solution, and the convection currents in the liquid. The concentration of the products of the reaction about the point, would tend to produce a ferrous reaction instead of a ferric reaction, and experi-

ment shows that a higher electromotive force is obtained with cells in which a ferrous reaction takes place than with those in which a ferric reaction occurs, and this change in the *character of the reaction* produced by the concentration probably accounts, at least in part, for the increased electromotive force at the point.

D. The iron salts about the point electrode.

The effect of artificially stirring the liquid, and the direct influence of the fluid condition of the solution on the deflections observed, at once suggested movements of the liquid, produced indirectly by the magnet. In order to locate these currents, and determine their potence, a small cell was made of two rectangular pieces of glass held by stout rubber bands to thick rubber sides. Perforations in the sides admitted the electrodes which were point and disc as before. The cell, between the poles of the electromagnet, was in a strong light, and the movements in the liquid were easily perceptible from the displacements of suspended particles introduced for the purpose. When very dilute nitric acid was placed in the cell, and the magnet excited, some interesting phenomena were observed.

The liquid, at first colorless, almost immediately assumed a pale brown color about the point, but nothing appeared at the disc electrode. The iron salts were drawn as soon as formed towards the point electrode, since here the rate of variation of the square of the magnetic force is a maximum.

As more iron was dissolved, a surface approximating to an equipotential surface of the pointed pole, and enveloping the colored iron salts, was observed enclosing the point, and at some distance from it. The outline of the surface became darker in a short time, and finally two or more dark contours, separated by lighter portions and symmetrical with the outer one, appeared between it and the point, indicating maxima and minima of density. When the magnetic field was gradually increased, this surface usually enlarged without breaking up and holding the iron salts within it. On further strengthening the magnetic field to about 16,000 H the ridges merged into one thick black envelope around the point.

This phenomenon is best studied with but little iron salts present, and by watching the point electrode with a microscope while the strength of the magnetic field is increased and decreased continuously. The sections, fig. 3 (p. 449), show the general form of these contours with different strengths of field.

Upon breaking the field, everything dropped from the point suddenly to the bottom of the cell, and on making the field again, it required a few seconds for the salts to reappear at the

point. This, at least partially, accounted for the sudden effects often noticed at breaking the field circuit, and the comparatively small ones at "make" especially with certain salt solutions, such as copper sulphate.

The outer envelope which held the iron salts together, and limited the immediate influence of the magnetized point, was distinctly defined within the liquid, and easily observed by the reflection of the light from its convex surface.

The persistency with which the iron salts were held about the point was shown by moving the cell with respect to the electrodes, when the contour remained approximately intact, passing bodily through the liquid without being broken up.

E. Electromagnetic rotations.

The small dust particles present in the liquid were drawn radially toward the point until they reached the surface described, when they pierced it and began to revolve rapidly about the point inside this surface, in the opposite direction to the currents of Ampère. Reversing the poles of the magnet, produced surfaces of the same appearance, but opposite rotations.

When the current from a Daniell cell was sent through, it seemed to have very little effect upon the rotations, showing them to be controlled by the powerfully magnetized point.

The electromagnet was arranged with its field vertical, and the point electrode along the lines of force as before. This arrangement gave better control of the surfaces formed, since gravity now acted symmetrically about the point.

When a single iron rod about 3^{mm} in diameter, and placed vertically in the cell, was substituted for the two electrodes, two rotations were observed, which were uniformly dextro about the north-seeking pole of the rod, and lævo about the south-seeking pole. About the central neutral portion no rotations were observed. When the rod was covered with a thin coating of vaseline, the rotations entirely disappeared as expected. Wartmann* observed similar rotations about soft iron cylinders adhered to the poles of a magnet, and he ascribed them to electric currents in the liquid which proceed from the periphery of the cell radially to the surface of the rod.

The explanation of these rotations follows at once from what we know of the time effects produced by the magnet. A higher potential is always produced at points of greater magnetization, causing electric currents in the liquid from the more strongly magnetized to the weaker parts of the iron.

* Philosophical Magazine, xxx, 1847, p. 268.

Applying this fact to the exposed conical point electrode, we see that local electric currents exist from its vertex to the other parts of the surface, returning by way of the metal. In the case of the vertical rod, these currents pass from the poles at its ends, through the liquid, to the neutral portions, returning as before.

These currents* under the influence of the poles themselves, would cause electromagnetic rotations of the liquid, as we find them. The mere mechanical influence of these rotations, as in the case when the liquid is artificially stirred, is to increase the chemical action upon the point, causing it to tend to act more like a zinc.

F. Acids which attack iron with the evolution of Hydrogen.

Professor Rowland had observed the "protective throw" with such acids to be extremely small and difficult to detect, except by very sensitive apparatus. The sensitive galvanometer was set up, and every precaution taken against inductive effects. A telescope and scale were used in this part of the work.

Several substances were first examined, among them being hydrochloric acid, acetic acid, perchloric acid, chlorine water, copper sulphate, ferric chloride, sulphuric acid, etc., but as these observations added nothing to the results already obtained, they are not given here.

After several trials a standard sulphuric acid solution was made up as follows:

Distilled water	10 grams
Gelatine	1 gram
C. P. Sulph. acid (sp. gravity 1·826)	1·062 grams

More strongly acidulated gelatine would not harden, and weaker solutions gave too small effects.

The "protective throw" was detected, but the point very soon became completely covered with minute bubbles of hydrogen, so that the electrodes had to be cleaned constantly.

The effect of adding hydrogen dioxide to the solution was next tried, since this would facilitate the removal of the hydrogen as soon as formed,† which was thought to act merely mechanically.

When about 1^{cc} of H_2O_2 was added to the solution, the "protective throw" became much more prominent, and the

* The rotations produced in liquids by axial currents, e. g. currents coinciding with the direction of the magnetic lines of force as distinct from radial currents, have been studied by Dr. Gore, Proceedings of the Royal Society, xxxiii, p. 151.

† J. M. Weeren, Berichte der Deutschen Chemischen Gesellschaft, No. 11, 1891.

gas bubbles only appeared in small quantities after a considerable time, further addition of small quantities of the dioxide showed the "protective throw" to be very decided with sulphuric acid when the hydrogen is removed from the surface of the electrodes in this manner.

G. The electromotive force.

Several attempts were made to obtain the relation between the strength of field and the electromotive force developed in the "protective throw," but it was difficult to obtain consistent readings owing to the trouble of balancing the original deflection, and the small absolute values of this electromotive force when hardened gelatine was employed.

A curve was constructed, however, showing the variation of the galvanometer deflection with the strength of field, using nitric acid solution without gelatine. This is shown in fig. 2, p. 449.

The readings were taken one after another, as rapidly as possible, to eliminate the damping effects of the iron salts formed.

The curve exhibits the general character of the variation. In the region from about 3,500 H to 8,000 H the greatest rate of change occurred, and beyond 10,000 H the curve became nearly horizontal for the particular electrodes used. Curves were also constructed for the "concentration throw" on making the field under different conditions, and they were approximately right lines more or less inclined, according to the amount of iron salts present.

With the sulphuric acid solution already given, the electromotive force varied from 0·0033 to 0·0078 of a volt, while with the nitric acid solution it became as great as 0·036 of a volt. In making all the solutions used with the different substances, amounts were taken proportional to their particular molecular weights, and then halved or doubled until of a suitable strength to give results with the galvanometer. It was thought possible at the beginning, that this might lead to some relations between the protective results and the strengths of the particular solutions, but the general irregular character of the whole phenomenon prevented comparisons in this respect, and all that can be stated is, that both the "protective throw" and the concentration effect, in general, increased rapidly with the strength of the solution.

H. Influence of a periodic magnetic field upon the cell.

An experiment was made to determine the behavior of the standard nitric acid cell when the magnetic field was made and

broken at regular intervals over a considerable time, and curves were drawn showing the variation of the "throw" with time, and the fluctuation of the original deflection caused by this treatment. The strength of field was about 11,000 H, and the experiment was conducted without compensating the original deflection, and by making the field for one minute, then breaking for one minute, and so on.

One of the curves is shown in fig. 1, (III) in which positive ordinates are values of the concentration throw at "make," and negative ordinates the values of the "protective throw."

Experimenting was not begun until the gelatine had completely hardened, and since the electrodes would tend to become polarized while the gelatine was hardening, the "protective throw" was very small, and soon masked by the concentration effects. After about five minutes, making the field had very little effect at all, but began to show decided "concentration throws" ten minutes later, and these rapidly increased with time, as the curve indicates.

Considering the fluctuation of the original deflection, the effect of this periodic field was to tend to reverse it, just as in the case of the uniform field in experiment B, but much more slowly, since the field was on but half the time in this case.

The cell also showed the iron salts almost entirely about the point, forming a thick black envelope.

I. Summary.—The principal results of this investigation may be summarized as follows:

Whenever iron is exposed to chemical action in a magnetic field, there are two *directly opposite* influences exerted.

(*a*) The direct influence of the magnetized condition of the metal, causing the more strongly magnetized parts to be *protected* from chemical action.

This is exhibited in the phenomenon of the "protective throw" which is always in the direction to protect the more strongly magnetized parts of magnetic electrodes. The "protective throw" is small, often requiring delicate apparatus to detect it, and is soon masked by the secondary concentration effects.

As to the absence of the "protective throw" with acids which attack iron with the evolution of hydrogen, the hydrogen acts merely mechanically, and when removed by adding to the solution small quantities of hydrogen dioxide, the "protective throw" becomes very decided.

In the curve, fig. 2 (p. 449), representing the variations of the "protective throw" with the strength of the magnetic field, we trace at once the magnetization of the point electrode. Since only the minute point was exposed to the liquid, it would

become saturated for comparatively small magnetizing forces, and the curve indicates that this occurred at about 10,000 H, beyond which the curve becomes practically horizontal. This further establishes the direct connection between this "throw" and the variation of the magnetization of the exposed point, and confirms the explanation of Professor Rowland, that it is due to the actual attraction of the magnet for iron, and not to any molecular change produced by magnetization.

(*b*) The indirect influence of the magnet caused by the concentration of the products of the reaction about the more strongly magnetized parts of the iron.

This tends to produce a higher potential at the more strongly magnetized parts, and finally establishes permanent electric currents, which go in the liquid from the more strongly magnetized to the neutral parts of the iron. This concentration effect increases rapidly with the amount of iron salts present and the fluidity of the solution.

The convection currents in the liquid are themselves a consequence of this same concentration, being electromagnetic rotations produced by the action of the magnet upon the local electric currents between different parts of the iron.

As to the permanent current, due to the magnet which is finally set up between the electrodes as shown in fig. 1 (II), it is probably due to a change in the character of the reaction produced by the concentration of the iron salts about the more strongly magnetized parts, which would tend to cause a ferrous instead of a ferric reaction to take place, and thus increase the electromotive force.

Physical Laboratory, Johns Hopkins University, May, 1892.

Note.—Since the completion of the above investigation, a number of experiments have been performed similar to those of Professor Remsen. Starting with the known existence and direction of the electric currents in the liquid, it was thought that these might lead to some explanation of the peculiar form of deposit in equipotential lines. A number of interesting facts have been noted, but they are withheld for further experiment. G. O. S.

ART. LIII.—*Nikitin on the Quaternary Deposits of Russia and their relations to Prehistoric Man;* by A. A. WRIGHT.

AT the international Congress of archæology in Moscow, in 1892, the Russian geologist, Mr. S. Nikitin, presented an elaborate paper upon the above subject. A summary of his views will be of interest in connection with the pending discussion upon the continuity of the Glacial epoch. The paper opens as follows: "The terms 'Quaternary Period' or 'Post-tertiary' with their subdivisions and geological equivalence in the series of deposits, are far from being definitely settled by science. At the latest sessions of the International Geological Congress at London and Washington there was much debate upon these questions without arriving at any definite results."

It will be recalled by those present at the Washington session that two distinct glacial epochs in Germany were argued for by Dr. Wahnschaffe,* and similarly by Baron De Geer for Sweden. On the other hand Professor Credner thought that the stratified beds between deposits of till were only local, indicating some retreat and re-advance of the ice-sheet, but no interglacial epoch. Dr. Carl Diener suggested that intercalated beds of sand were no positive proof of interglacial epochs, as moraines, in the Austrian Alps, no more than twenty years old, were covered with pasture. Dr. Holst of Sweden, mentioned two moraines separated by interpolated sand, and thought that they might both have been formed by the same ice-sheet. A blue ground-moraine and a yellow upper-moraine were deposited even in northern Sweden, where there is no indication of the retreat of the ice. Professor Hughes of Cambridge, expressed his opinion that the Ice age was a single continuous cold period, in England at least, except for slight and unimportant oscillations in the extent of the ice-sheet.

Mr. Nikitin continues: "I do not pretend to solve this complicated question; but will confine myself to giving a brief analysis of the signification and the meaning which I attribute to this terminology. Under the name of Quaternary period or Post-tertiary I include all the time since the close of the Pliocene up to our day. I divide this period into two epochs, the Pleistocene (earlier) and the modern epoch. The close of the Pleistocene is characterized, as I conceive, by the disappearance of the mammoth, the rhinoceros, and other large mammals which are now wanting within the limits of Russia. This subdivision coincides with that of many archæologists

* Am. Geol., viii, 241.

that is to say, with the subdivision into the *palæolithic* and *neolithic* epochs. . . . . I think that this subdivision will stand, even though, along with the remains of the mammoth, there should be found some polished stones as the first indications of a more perfect industry." . . . .

"As to the time of the disappearance of the mammoth . . . it is certain that wherever the glacial deposits are developed in their entirety, the remains of the mammoth are not found above the morainic deposits of the so-called second glaciation; or at least they are very rare. The time of the greatest development of the mammoth and rhinoceros in Europe corresponds to the period called interglacial, and to the second glaciation of northern Europe. In northern and central Russia, which exhibits everywhere but a single moraine, the remains of the mammoth and rhinoceros are found principally in loessiform deposits, in old lake and river deposits covering the moraine, or the products of its alteration. These facts prove that the morainic deposits of Russia belong to the first glaciation, and that by analogy with the west our loess, and the ancient alluviums where the remains of the mammoth and rhinoceros are found, are sediments corresponding to the interglacial epoch, and the second glaciation."

"There are two questions whose solution is important for the subject of which I am treating: first, that of *two glaciations* in middle Europe, and then, that of the so-called *interglacial deposits* of Germany, England and Scandinavia. You know, gentlemen, that the idea of two epochs of glaciation (and even of several, according to some investigations) has been suggested by the discovery, upon the great expanse of the countries mentioned, of two morainic deposits, separated by heavy, stratified beds, in which are occasionally found numerous traces of the Pleistocene fauna and flora. At the same time, the partisans of this theory affirm that the second glaciation was less powerful than the first, and that it could not cover all the region occupied by the primary and principal glaciation. You know also, gentlemen, that this theory, adopted by the larger number of those who have studied the Quaternary deposits, is far from being irrefutable. I will remark in the first place, that the supposition of three and even four distinct glaciations instead of two, indicates the possibility of diverse explanations, and diverse opinions upon the genesis of these interglacial deposits. For several countries, there has recently been demonstrated the weakness of the proofs which have been used in affirming the existence of several Glacial epochs, separated by periods whose climatic conditions have been entirely different. Contemporary geological literature furnishes us with some examples which demonstrate that there has been an error,

even in the case of certain classical sections of interglacial deposits, so that these have now lost the importance that was formerly accorded to them." . . . .

"In 1885 I made a visit to Germany, for the purpose of comparing these Post-tertiary deposits with the corresponding deposits of Russia. The results of my journey were then published in Russian, and later were compiled by Mr. Sjögren in German and in Swedish, so that they have become accessible to the savants of western Europe. Among other things, I prove in those reports a complete analogy between the Russian Quaternary deposits and the German types; with only this difference, that over a vast expanse in central and northern Russia there is a complete absence of traces of interglacial deposits, and of the moraine of the second glaciation; and that the eastern limit of the second glaciation must pass through Lithuania and the Baltic region. It is true, that in the detailed geological literature of Russia we frequently find announcements of the discovery of interglacial beds at one point or another in middle Russia, or even in southern. Nevertheless, none of these cases can be taken seriously, as I believe. Often they are called forth only by the false idea that all the details of the Quaternary deposits of northern Germany ought to be discovered everywhere in Russia." . . .

Proceeding to describe with more detail the deposits of certain districts, he enumerates the four following as the principal strata in Finland:

(*a*) Old stratified sands and clays, intercalated in a few places between the crystalline rocks and the moraine.

(*b*) Unstratified clays, clayey sands and pebbly moraine, mostly blue (*grises*) with polished, sub-angular, striated blocks —the *moraine profonde* of the first glaciation, according to the Swedish classification.

(*c*) Stratified sands and clays, with some rounded gravel—the "interglacial" beds.

(*d*) Unstratified, clayey gravel, sand and clay, mostly yellow, with morainic pebbles and bowlders—the *moraine profonde* of the "second glaciation." In discussing the age of these deposits he says:

"As to the advance of the glacial epoch in Finland and the time of the formation of the two morainic clays, the terminal moraines and osars, nothing is yet known with certainty. However, we have as yet no reason to distinguish here, as a fact irrevocably proved, the deposits of the first glaciation, interglacial deposits, and those of the second glaciation, as in Germany and Scandinavia. All the phenomena known up to the present time connected with the glacial deposits of Finland can easily be explained by a single, continued glaciation,

and by a single glacier subject to oscillation. In short, no interglacial deposits are here known containing animal and vegetable remains. The morainic clay of the type (*b*) alone is distributed over the interior of the country, and only in the border portions of the country does it seem to be separated into two types (*b*) and (*d*)."

The author gives summary accounts of the deposits in seven different regions, as follows:

1. Finland, and the government of Olonetz.
2. The Baltic region and the Waldaï Mountains.
3. Poland and Lithuania.
4. Central Russia.
5. The region of morainic deposits near the limits of their distribution.
6. The region of steppes in southern Russia, beyond the limits of glaciation.
7. The southeastern region of Russia.

The whole makes a pamphlet of thirty-four large octavo pages. It is, however, only the summary of a more detailed report which he is soon to publish. It closes with the following:

"*Principal Theses.*"

1. "The subdivision of the stone age into palæolithic and neolithic epochs should be preserved for European Russia, because it here coincides with the geological divisions into Pleistocene and modern, which are in their turn based upon palæontological data.
2. "The study of the glacial deposits of Finland and of the western region furnishes no proof of the existence of two distinct glacial epochs and an interglacial epoch. All the facts can be explained by the phenomena of the oscillation of the glacier at the time of its gradual, but irregular, retreat.
3. "If however one accepts the Swedish and Prussian theory of the subdivision of the glacial period into two epochs and an interglacial epoch, the second glaciation cannot have extended beyond the western region, in a certain part (comparatively restricted) of the Baltic region, of Finland and of the government of Olonetz.
4. "The other portion of Russia subjected to glaciation, has only one morainic stage, corresponding to the deposits of the first glacial epoch of the Swedes.
5. "At the epoch of the more extended glaciation the major part of Russia presented the aspect of a desert of ice, similar to that of Greenland, carrying no moraine upon its surface, and presenting no elevation free from ice, where forest vegetation could be preserved.

6. "The time corresponding to the interglacial epoch and the second glaciation of the Swedes, was probably, for the greater part of Russia, the epoch of the formation of the ancient lake deposits, the loess, and the upper terraces of the rivers, which constitute the principal repository for the bones of the mammoth and other extinct mammals, which abounded here while Scandinavia and Finland were still covered by the glacier.

7. "In accordance with the composition and genesis of her Quaternary deposits, European Russia may be divided into a series of typical regions which are very characteristic, although resting upon differences which are scarcely recognizable, but which illustrate none the less the life of the immense Russian plain during the Quaternary period, and the formation of her superficial deposits.

8. "In the second portion of the Glacial epoch, or of the pleistocene, the mammoth and other large mammals inhabited southern and eastern Russia in great numbers. As the glacier retreated these animals advanced toward the north and northwest; toward the close of the pleistocene they reached Finland for a very short time, and then disappeared entirely throughout the whole extent of European Russia, but probably later in its northeastern part and in Siberia.

9. "Man lived contemporaneously with the mammoth during the second part of the glacial epoch along the limits of glaciation, possessing an industry well advanced, and making use of fire among other things, but producing implements solely of flaked flint. As the glacier retired, man advanced toward the north and northwest: he arrived in Finland and the Baltic region after the close of glaciation and after the disappearance of the mammoth; but man himself possessed already the more advanced culture of the neolithic age, and besides implements of trimmed flint, he knew how to make implements in polished stone, pottery, etc.

10. "European Russia shows no traces of man in the first part of the Pleistocene, or of any more ancient man."

ART. LIV.—*Rigidity not to be relied upon in estimating the Earth's Age;* by OSMOND FISHER, Cambridge, England.

IT is impossible not to admire the ingenious argument by which Mr. Clarence King* reasons that, assuming the earth to be rigid, the temperature gradient must be such that, within the first few hundred miles at least, it cannot intersect the curve which he uses to express the fusibility of igneous rock under the pressure corresponding to the depth. Placing this before his mind, he was led to obtain an examination of the rock diabase at high temperatures to be made by Dr. Barus;† and we owe a debt of gratitude to both these gentlemen for an interesting addition to our scanty store of knowledge of this obscure class of subjects.

On comparing Dr. Barus's results with those obtained by Professors Rücker and Roberts-Austen for the dolerite of Rowley Regis, we are struck by the considerably higher value of the melting point of diabase, which is about 1170° C., whereas that of the dolerite was found to be under 920° C. On the other hand, Dr. Barus makes the latent heat of fusion of the diabase to be 24, whereas that of the dolerite is 49;‡ thus the latent heat of the rock which has the lower melting point is more than double that which has the higher.

When, however, by means of the above considerations Mr. King endeavors to fix a limit within which the age of the earth must lie, it is clear that the rigidity of the earth must be first established. In proof of this he refers to the "unshaken results of Ld. Kelvin (Sir W. Thomson) and Professor G. H. Darwin," and to "the further arguments for rigidity advanced by Professor S. Newcomb§ from the data of the lately ascertained periodic variation of terrestrial latitude, as together warranting a firm belief in the rigid earth."

I hope it will not be thought presumptuous if I endeavor to point out what these authorities have really determined. And first of Professor S. Newcomb's discussion of the periodic variations of latitude.

On referring to the article in the monthly notices of the Royal Astronomical Society,§ it will be found that he proposes two modes of explaining the phenomena. The first hypothesis which he examines is an elastic yielding of the solid earth, and he comes to the conclusion, that the phenomena recently dis-

* This Journal, Jan., 1893. † *Ibid*, Jan., 1892.

‡ Appendix to the writer's "Physics of the Earth's Crust," 2d ed., p. 18, 1891. See also the account of the experiments, Phil. Mag., Oct., 1891.

§ For March, 1892.

covered may be accounted for in that manner, if the earth is slightly more rigid than steel; but he does not stop at this explanation. He goes on to say, "we have next to consider the effect of viscosity of the earth. Those geologists, who have given special attention to the subject, regard it as well established, that the earth yields under the weight of deposits, as if it were a thin crust floating upon a liquid interior, and must therefore be a viscous solid, if a solid at all." He then states, that the phenomena observed might in such a case be produced, if some disturbing cause acted, adding, "a *vera causa* was pointed out some years ago by Sir William Thomson in the motions of the winds and oceans, and especially in changes in the polar ice cap." Thus it appears that Professor Newcomb does not consider that there may not be a possible alternative to the hypothesis of steel-like rigidity; and evidently he does not regard the question as settled, for the concluding words of his paper are, "but under the actual circumstances we must await the results of further investigation into the whole subject."

Professor Newcomb tells us that, in the case of a viscous earth, "the poles [of rotation and figure] would eventually appear to meet, unless separated from time to time by [disturbing] causes changing one or both of them." A geologist acquainted with the flow of solid rock would hardly recognize a condition of the interior so elastic, and so devoid of viscosity, that during geological ages the elasticity would be constantly maintained, so that this coincidence of the poles should not by this time have been accomplished. If this be so, then the action of disturbing causes is still needful to account for their separation at present, and there is no stronger argument from variation of latitude for an elastic earth than for a viscous or liquid interior.

While referring to authorities it is worth while to mention that Professor Harkness, in his exhaustive work "On the Solar Parallax and its related Constants including the Figure and Density of the earth," remarks, that, "Notwithstanding the difficulties which arise in connection with the rigidity of the earth under the action of the forces which generate precession, nutation, and the tides, the theory of a comparatively thin crust resting in approximate hydrostatic equilibrium upon a denser substratum is favored by enough facts to render it very plausible."*

Let us now turn to what Mr. King describes as "the hitherto unshaken results of Ld. Kelvin and Professor G. H. Darwin" as to the tidal rigidity of the earth. It is no doubt a very serious matter to hold an opinion opposed to such high author-

* Washington, Government printing office, 1891, p. 143.

ities in physics, especially when backed by experienced geologists like Messrs. Clarence King and G. F. Becker: nevertheless I pray *audi alteram partem*.

It will, I think, be at once admitted that these objections to a yielding earth have been based upon the equilibrium theory of the tides. It does not seem impossible that the equilibrium theory may give a fairly good approximation to the truth in the case of the bodily tides of the earth itself, although the moment of inertia, and the forced period of oscillation differing from the gravitational, must give rise to deviations from the exact equilibrium value of the tidal distortion. But let us assume that the bodily tide agrees with the equilibrium theory. Then the pith of the objection to a yielding earth is well summarized in Ld. Kelvin's words, "Had the solid part of the earth so little rigidity as to allow it to yield in its own figure very nearly as much as if it were fluid, there would be very nearly nothing of what we call tides—that is to say rise and fall of the sea relatively to the land, but sea and land together would rise and fall a few feet every twelve lunar hours. This would, as we shall see, be the case if the geological hypothesis of a thin crust were true."* But this statement of the question rests on the equilibrium theory of the tides, and takes no account of the horizontal motion of the water to which its accumulation at high and diminution at low tide are due. As Airy wrote, "the problem of the tides, it is evident, is essentially one of the *motion* of fluids;"† and again (one almost hesitates to quote the words), "it must be allowed that it is one of the most contemptible theories that was ever applied to explain a collection of important physical facts. It is entirely false in its principles, and entirely inapplicable in its results."‡

The hydrodynamical problem has never been treated fully on account of its complexity, but for tides of short period the canal theory is thought to give results most nearly in accordance with nature. Now, the only investigation of the tide upon a yielding earth according to the canal theory with which I am acquainted is given by Professor Darwin§ but he has left his result in general symbols without reducing it to a numerical estimate. It is, however, perfectly easy on certain assumptions to supply this desideratum, all the quantities involved having known astronomical values except two. These two are the height of the bodily tide, and the amount of its lag. Let us then suppose the earth's interior to consist of a liquid of small viscosity, which is the case in which the ocean tide ought to be most diminished. In that case the bodily tide

* Thomson and Tait's Natural Philosophy, § 833.
† Encyclopædia Metropolitana, "Tides and Waves," § 14.
‡ Ditto, § 64.
§ Phil. Trans. Part I, 1879, p. 23.

may be taken at the equilibrium value, which for a large body like the earth is very much more suitable than it is to a layer of water like the ocean. The height of such a lunar tide is estimated to be about $1\frac{3}{4}$ feet from highest to lowest,* and the lag would be small. The diminution of the tide from its normal amount is caused by the attraction of the two bodily protuberances, and these must be taken as of half the mean density of the earth. Introducing these values into Darwin's formula I have obtained the result† that the tide would be diminished by only one-fifth of what its height would be on a rigid earth. If for instance the height would be fifty inches on a rigid earth, it would still be forty inches if the earth was liquid. Now, since we do not know what the precise height of a tide on a rigid earth would be, it is quite possible that the tides we actually experience may be of the height appropriate to a liquid interior, seeing that the diminution would be so small.

If there is no flaw in the above reasoning, the rigidity of the earth has not been established by the argument from the tides of short period, and no estimate of the earth's age can be based upon a belief in such a condition of the interior derived from their existence. If, however, the argument is transferred to the fortnightly tide, the reply may be made that there is no certain evidence from observation of the existence of such a tide; for "it is certain that, if at a given port a tide exists, the average height of that tide ought to be always the same year by year, and its lag ought to be the same. But in fact the average annual height of the fortnightly disturbances of the sea at Karachi, in India, which is the port where the necessary observations have been carried out for fifteen years, does not maintain anything like a constant value. This appears to show that no conclusion can be drawn from the observations to decide the question whether there is such a tide or not. The disturbances may be wholly due to meteorological causes. At any rate, if such a tide exists, it is so masked by meteorological disturbances as to be unrecognizable. The irregularity of the times of disturbances is equally noticeable

* Thomson and Tait's Nat. Phil., 2d Ed. § 804. Mr. King, p. 17, writes as if the tidal deformation of the earth would be five feet if it is not rigid, but does not give his authority. Possibly he may be referring to the observed height of the tide at oceanic islands, which on the assumption that the tide would be obliterated by a yielding earth would afford a measure of the yielding. The only numerical estimate I have been able to find is in "Thomson and Tait," and is that which I have given above. If any larger one is mentioned I have overlooked it.

† See a paper by the writer on "the hypothesis of a liquid condition of the earth's interior considered in connection with Professor Darwin's theory of the Genesis of the moon." Proc. Cam (England) Phil. Soc., May 30, 1892.

with the irregularity of their amount."* The mean of all the heights is 0·396 inch. The least annual mean is 0·072 and the greatest 0·936; the difference between them, 0·864, is more than double the mean of the whole series of observations, which indicates the existence of a disturbing cause of the same order of magnitude as the quantity to be measured, so that we can draw no inference either way.

I submit, therefore, that the title of this article has been justified, and that it has been shown that rigidity cannot be relied upon as affording a datum towards estimating the earth's age.

Art. LV.—*On the Treatment of Barium Sulphate in Analysis;* by J. I. Phinney.

[Contributions from the Kent Chemical Laboratory of Yale College—XXIII.]

In a recent paper by M. Ripper† entitled "Beiträge zur Gewichtsanalyse der Schwefelsäure" the method discussed is the precipitation of barium sulphate from an excess of the chloride and differs from similar methods only in the manner of purification of the precipitate. Purification according to Ripper, is accomplished by oxidizing with bromine water whatever sulphate may have been reduced by the ignition of the filter, then treating the entire precipitate with dilute hydrochloric acid until the impurities are removed. In the course of his investigation Ripper made the attempt to eliminate the possible source of error in the reduction of the sulphate by the use of the asbestos filter-crucible, but finding it impossible to bring asbestos to a sufficiently constant weight either by itself or when treated with dilute acid, he abandoned it as impracticable, and substituted the treatment of the reduced precipitate with bromine. Ripper accepts without investigation the old method of purifying barium sulphate by hydrochloric acid.

Inasmuch as the asbestos crucible has been employed successfully even in processes so delicate as atomic weight determinations, sufficient confidence was felt in it to warrant testing by its use the accuracy of the hydrochloric acid process of purification, in this way reducing the necessary manipulation and completely avoiding the introduction of bromine. Further-

* Appendix to the writer's "Physics of the Earth's Crust," 2d ed., p. 34, where a table of the annual heights and lags are given, compiled from the "Results of the Harmonic Analysis of Tidal Observations," by Major Baird and Prof. Darwin, Proc. Roy. Soc., vol. xxxix, p. 135, 1886.

† Zeit. f. anorgan. Chem., ii, 36.

more the recent work done in this laboratory by Drs. Mar and Browning* on barium sulphate depends for its validity upon the practical utility of this means of gathering and weighing barium sulphate. Accordingly the following preliminary series of experiments were undertaken with a view of discovering under what conditions and how far the asbestos crucible could be depended upon in quantitative methods as applied to the estimation of barium as sulphate. In Series I the crucible with a felt was ignited to bright redness for different periods of time and weighed, then washed with hydrochloric acid, both cold and hot, ignited, and re-weighed with results as shown below. The crucible used was finely perforated and furnished with a cover and cap, and the asbestos was prepared as directed by F. A. Gooch,† in his original paper. A felt weighing 0·0258 grm. was thrown upon the crucible, washed thoroughly with distilled water, dried, ignited, and weighed in less than twenty minutes. The formation of blisters due to rapid generation of steam was easily avoided by gradually increasing the temperature from a gentle heat. A second crucible with a felt weighing twice as much (0·0441 grm.) was ignited at low redness for equal periods with similar results.

SERIES I.

Time of ignition.	Weight in grams.	Time of ignition.	Weight in grams.
2 min.	0·0258	10 min	0·0258
2 "	0·0258	10 "	0·0258
2 "	0·0258	20 "	0·0258
5 "	0·0258	20 "	0·0258
5 "	0·0258	30 "	0 0258

The same felt was washed with 20 cm^3 of a twenty-five per-cent solution of hydrochloric acid, then treated with 5 cm^3, 25 cm^3 cold, and 25 cm^3 hot concentrated acid respectively, and suffered in no case the slightest diminution in weight, constant weights being secured after an ignition of two minutes. Finally as a matter of curiosity rather than because of its practical bearing the felt was digested in the crucible for fifteen hours in concentrated acid, washed with 100 cm^3 distilled water, and even then lost but 0·0001 grm. The stability of the asbestos under the foregoing treatment is remarkable. An excessive ignition for nearly two hours at bright redness gave no appreciable change, while in the last experiment the trifling loss may perhaps be accounted for by mechanical disintegration.

In Series II, barium sulphate brought to a constant weight was treated with acid on the felt without difficulty—in the first two cases with a few drops of dilute hydrochloric acid followed

* This Journal, xli, 288; xliii, 314; xliv, 450.
† Amer. Chem. Jour., i, 317.

by 10 cm³ of distilled water, in the third, with 100 cm³ of a three per cent solution of the acid—though Ripper raises the further objection, that upon ignition the precipitate becomes so firmly attached to the felt that it is nearly or quite impossible to make a thorough treatment with acid. In experiments (1) and (2) no attempt was made to pulverize the precipitates, but in experiment (3), as also throughout Series III, on moistening with a few drops of water the sulphate was easily and completely disintegrated by a glass rod into finely divided particles. This difference in treatment explains, at least in part, the large difference in the results of the following table.

SERIES II.

$BaCl_2 \cdot 2H_2O$ taken.	Time of ignition.	$BaSO_4$ found.	Error.	Treatment with acid.	Weight after treatment.	Loss.
grm.		grm.	grm.		grm.	grm.
(1) 0·5071	10 min. 20 "	0·4848	0·0003 +	4–5 drops HCl 4–5 " HCl	0·4845 0·4845	0·0003 0·0000
(2) 0·5022	10 " 20 "	0·4799	0·0001 +	4–5 " HCl 4–5 " HCl	0·4796 0·4793	0·0003 0·0003
(3) 0·5007	5 " 5 "	0·4783	0·0001 −	100 cm³ 3 per cent HCl	0·4751	0·0032

The filtrates in experiment (2) gave with an excess of sulphuric acid slight unweighable precipitates, but from the filtrate of experiment (3) 0·0030 grm. of the sulphate were recovered. The disintegrated residue from experiment (2), (0·4793 grm. $BaSO_4$), was next treated under precisely the same conditions as in the last preceding experiment except that in this solution there was present dilute sulphuric acid amounting to five percent of the entire volume, an excess sufficient to keep the barium in the form of sulphate.* In this case there was no loss in weight nor did the filtrate contain any barium.

This work completely demonstrates not only that strong hydrochloric acid has no effect upon the film of asbestos, but also that barium sulphate when thrown upon it may be brought to a constant weight either by itself or after treatment with dilute acids, and incidentally that the requisite excess of sulphuric acid must be present to counteract the solvent effect of the hydrochloric acid. That Ripper failed to secure constant weights is probably due to unfamiliarity with the proper sort of material to be used.

In view of the facts thus far ascertained the next step was to purify the sulphate, if possible, by the means already referred to in the beginning of this paper. The contaminating salts chosen were potassium chlorate and sodium chloride, as those

*Fresenius, Zeit. f. anal. Chem., xxx, 455

most likely to present a fair test of the efficacy of the process. The following precipitations were made:

No.	$BaCl_2 . 2H_2O$ taken. grm.	$BaSO_4$ found. grm.	Error. grm.	Contaminating salt. grm.
1.	0·5008	0·5009	0·0224 +	$KClO_3$, 3
2.	0·5014	0·4990	0·0198 +	$KClO_3$, 3
3.	0·5007	0·4980	0·0196 +	NaCl. 10
4.	0 5004	0·5165	0 0384 +	NaCl. 20
5.	0·5012	0·4979	0·0190 +	$KClO_3$, 3

By reference to the following table in which the records of treatment of these precipitates are given in their numerical order, it will be seen that the action of hydrochloric acid in the presence of sulphuric acid is to remove only from 70 to 90 per cent of the total impurity, and that, while it is possible by repeated treatments with dilute hydrochloric acid alone to so reduce the weight that there may be little or no apparent error on the original determination, the large percentage of sulphate dissolved at the same time condemns its use in accurate analytical work.

SERIES III.

	Acids used in total vol. of 100 cm³. HCl cm³	H_2SO_4 cm³	Duration of acid treatment.	Loss on treatment. grm.	Impurity remaining. grm.	$BaSO_4$ recovered by H_2SO_4 in filtrate.
1.	3	5	30 min.	0·0175	0·0049	none
	3	5	15 "	0·0012	0·0037	"
	3	5	15 "	0·0012	0·0025	unweighable trace
	3	5	15 "	0·0000	0·0025	" "
	3	5	15 "	0·0003	0·0022	" "
	3	0	15 "	0·0031	0·0009 —	0·0020 grm.
2.	3	5	20 "	0·0135	0·0063	none
	3	5	20 "	0·0015	0·0048	"
	3	5	20 "	0·0003	0·0045	"
3.	3	5	30 "	0·0090	0·0106	none
	5	10	20 "	0·0013	0·0093	"
	10	10	20 "	0·0023	0·0070	"
	25	10	20 "	0·0002	0·0068	"
	50	10	15 "	0·0002	0·0066	"
4.	90	10	15 "	0·0260	0·0124	none
	90	10	15 "	0·0009	0·0115	"
5.	3	0	30 "	0·0146	0·0044	0·0007 grm.
	3	0	30 "	0·0040	0·0004	0·0032 "

Fresenius states* that barium sulphate impure from sodium or potassium chlorates may be completely purified by igniting the precipitate, moistening thoroughly with hydrochloric acid. evaporating to dryness and extracting with water, and that

* Zeit. f. anal. Chem., ix, 62.

chlorides of these elements bring about no contamination. However, in the above series of precipitations the inclusion by the sulphate of sodium chloride and potassium chloride (left on ignition) was very marked, and accordingly four new precipitations were made, two in the presence of 10 grm. of sodium chloride, and two with an equal amount of potassium chloride as the contaminating salt, in order to test the degree of purification reached by Fresenius' process. The evaporation was made over a steam bath and hot water was used in washing. It was found an easy matter to remove the precipitates from the felts after ignition by breaking up the caked mass with a glass rod by a rotary motion and gently tapping the crucible. After extraction the residue was thrown back upon the same felt, ignited, and re-weighed with results as below:

I.

$BaCl_2 . 2H_2O$ taken.	$BaSO_4 + NaCl$ found.	Impurity before treatment.	Loss on treatment.	Impurity remaining.
0·5000 grm.	0·4955 grm.	0·0177 grm.	0·0079 grm.	0·0098 grm.
0·5003 "	0·4973 "	0·0193 "	0·0100 "	0·0093 "

II.

$BaCl_2 . 2H_2O$ taken.	$BaSO_4 + KCl$ found.	Impurity before treatment.	Loss on treatment.	Impurity remaining.
0·5033 grm.	0·5024 grm.	0·0215 grm.	0·0131 grm.	0·0084 grm.
0·5017 "	0·5071 "	0·0277 "	0·0189 "	0·0088 "

Under the most favorable conditions an average of 0·0090 grm. of the total impurity in a half-gram of the impure sulphate remained untouched, and in one case a retreatment diminished this amount by only 0·0004 grm. Slight precipitates were recovered from the filtrates of II, the first weighing 0·0001 grm. and the second unweighable.

We are forced, then, to the conclusion that alkaline chlorides do contaminate barium sulphate thrown down in the presence of an excess of sulphuric acid* and that the process of purifying by hydrochloric acid does not purify. It would seem therefore that the only good method for purification is either to fuse, according to Fresenius, with sodium carbonate, extract and reprecipitate as sulphate, or to evaporate from solution in concentrated sulphuric acid according to Mar.†

In conclusion, the author desires to acknowledge the suggestions and help of Prof. F. A. Gooch freely given throughout these investigations.

* See also this Journal, xli, 288. † Ibid.

ART. LVI.—*The Validity of the so-called Wallala Beds as a Division of the California Cretaceous;** by HAROLD W. FAIRBANKS, F.G.S.A., Berkeley, Cal.

THE classification of the California Cretaceous, as given by Dr. C. A. White in Correlation Papers—Cretaceous, is as follows:

Lower Cretaceous.	Shasta Group.	Knoxville Beds. Shasta Beds.
Upper Cretaceous.		Wallala Beds. Chico.

The designation Wallala as applied to a supposed new division of the California Cretaceous was given by Drs. White and Becker to some beds discovered during the investigations for the monograph on the Quicksilver Deposits of the Pacific Slope. These occur on the coast of Mendocino Co. near Ft. Ross, and consist according to Dr. Becker of a series of shales, sandstones, and conglomerates, some thousands of feet in thickness, and in character closely resembling the Chico as it is known in other parts of the State. Dr. Becker states that the beds rest unconformably on the Metamorphic Series, but that the stratigraphical position with reference to the Chico is not shown. According to Dr. White the beds are older than the Chico but younger than the Shasta Group. The evidence with regard to the exact position of the strata is wholly paleontological and it is on this that he has established the division.

The fossils found were in bad condition but the following genera were made out: *Ostrea*, *Inoceramus*, *Pecten*, *Cylichna*,

* Since this article was prepared for publication there appeared in the American Geologist a resume of a paper read at the last meeting of the Geological Society of America in Ottawa, Canada, by J. S. Diller, entitled: The Cretaceous and Tertiary of the Pacific States; and also of one by T. W. Stanton on the Faunas of the Shasta and Chico Formations. The authors of these papers arrived at substantially the same results as I have expressed in this article with regard to the validity of the Wallala beds. This is interesting because of the different fields studied and of the entire independence, each of the other, in the conclusions reached. I was not aware that any one else was engaged in such a study.

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Mesozoic and Cenozoic Paleontology of California, Bull. U. S. Geol. Sur., No. 15. C. A. White.

Notes on the Stratigraphy of California, Bull. U. S. Geol. Sur., No. 19. G. F. Becker.

On New Cretaceous Fossils from California, Bull. U. S. Sur., No. 22. C. A. White.

Geology of the Quicksilver Deposits of the Pacific Slope, by G. F. Becker.

Geology of Baja, California, Proc. Cal. Acad. Sci., 1888, by W. Lindgren.

Correlation Papers—Cretaceous, Bull. U. S. Geol. Sur., No. 82, by C. A. White.

Turritella, *Solarium*, and one subsequently determined as *Coralliochama orcutti*. The Coralliochama is the type of a new genus and is the most characteristic fossil in the Wallala beds as well as in those on Todos Santos Bay.

About the same time C. A. Orcutt of San Diego sent to the National Museum a collection of fossils from the shore of Todos Santos Bay, Lower California. These were in a good state of preservation and included the following species: *Coralliochama orcutti*, *Nerita*, *Cerithium pillingi*, *C. totium-sanctorum*, and *Trochus euryostomus*. The Coralliochama is thus seen to be the only species common to both localities, the other species being new.

Although the two occurrences are so widely separated, Dr. White found a general resemblance of the faunas, and as they were different from any known Cretaceous in the United States and resembled the Gosau of Europe, he termed the whole the Wallala beds. Wallala being a town near the occurrence in northern California. The latter beds I have not seen, but the past year an opportunity was given me to examine those on Todos Santos Bay. The strata, consisting of shales, sandstones, and conglomerates resembling the Chico, are exposed in cliffs along the southern shore of the bay for about three miles. They form a narrow strip along the north flank of Punta Banda, a long high ridge of porphyry and diorite bounding the bay on the south. The strata dip to the northeast at an angle of 30–60 degrees and are somewhat faulted but are entirely unaltered. Fossils are not abundant through the formation but a considerable variety was collected during my hasty visit. The Coralliochama is exceedingly abundant in strata scattered through a vertical distance of several hundred feet. One bed four feet thick was formed almost wholly of a mass of shells. The following is a list of the fossils found here.

Coralliochama orcutti.
Axinæa veatchi.
Ostrea ——
Pugnellus ——
Astartate mathewsoni.
Venus varians.
Fusus ——
Leda translucida.
Turritella chicoensis.
Tellina ooides.
Mactra ashburneri.
Tellina æqualis.
Lunatia avellana.
Volutilithes ——
Actæonina pupoides.
Cinulia obliqua.
Nucula truncata.
Baculites chicoensis.
Gyrodes expansa.
Ancyloceras lineatus.
Leda gabbi.

It will be seen that not only is this list much larger than that found by Mr. Orcutt but with the exception of the Coral-

liochama it is wholly different. The fauna very closely resembles the Chico as it is known in California.

During the course of several months spent in the vicinity of San Diego I made a careful study of the unaltered shales, sandstones and conglomerates along the coast. This resulted in a large collection of Tertiary and Cretaceous fossils, many of the latter being new species. The most important result of this study, however, was the proof of the actual relation of the supposed Wallala beds to the Chico; a relation which seemed probable from the fauna found on Todos Santos bay, but which at San Diego was shown both paleontologically and stratigraphically. These Cretaceous beds were found at two points on the coast, one at La Jolla the other on Pt. Loma. The latter is a long high peninsula partly inclosing the bay of San Diego. It is almost precipitous and good sections of the strata are exposed. They consist of shale and sandstone with an unconformable late Tertiary conglomerate overlying. The peninsula is formed by a local uplift, and though the strata are not greatly inclined the amount of faulting has been remarkable. There are probably not less than four hundred to be seen along a distance of four miles on its seaward face.

Dr. J. G. Cooper many years ago obtained three species of Chico fossils from this peninsula, one being an Ammonite, found in a shaft sunk for coal. No published notice was ever made of this discovery except the original descriptions in Gabb's Palæontology of California, Vol. I, pp. 69, 80 and 197. The strata dip generally to the northeast at a small angle except at the very southern extremity of the peninsula where they are reversed and dip southerly, thus forming an anticlinal with the lowest strata near the end. The peninsula lessens in height to the northeast in the direction of False Bay under which the strata seem to dip, reappearing again on the opposite side toward La Jolla, the bay lying in the synclinal. The *Coralliochama orcutti* and several other species occur in a sandstone at the base of the cliffs and almost covered by the water at high tide. The Tertiary conglomerate is fully three hundred feet thick at the extremity of the point, and consists partly of bowlders similar to the crystalline rocks in the mountains east, and partly of sandstone bowlders many of which contain specimens of the Coralliochama, Cephalopods, and well known Chico forms. The conglomerate completely covers the sandstones on the inner side of the extremity of the point, but since all the fossils found in place are similar to those in the bowlders and the bowlders themselves are lithologically similar to the rocks in place, there seems not the slightest doubt but that they all belong to the same formation,

the richest fossiliferous portions being covered by the conglomerate. The Coralliochama is fairly abundant in places but is poorly preserved. The following is a list of the fossils found in place and in the bowlders. These fossils as well as those in the other two lists given in this article were determined by Dr. J. G. Cooper. The original descriptions with two or three exceptions were by Gabb.

Actæonina pupoides.
Actæonina —— n. s.
Ammonites whitneyi.
Ampullina striata.
Angaria ornatissima.
Arca breweriana.
Astarte mathewsoni.
Callistoma —— n. s.
Cardium placerensis.
Cerithium pillingi.
Cerithium —— n. s.
Carbula —— n. s.
Crassatella tuscana.
Crassatella —— n. s.
Crenella —— n. s.
Haliotis —— n. s.
Lima microtis.
Lithophagus oviformis.
Heteroceros cooperi.
Lucina postradiata.
Lunatia conradiana.
Meretrix arata.
Patella traski.
Pecten californicus.
Perissolax brevirostris.
Pholadomya breweri.
Puncturella —— n. s.
Tapes quadrata.
Trapezium carinatum.
Tritonium —— n. s.
Ancillaria elongata.
Architectonica horni.
Avicula pellucida.
Bulla —— n. s.
Conus horni.
Conus rémondi.
Dentalium cooperi.
Dosinia —— n. s.
Meretrix horni.
Meretrix uvasana.
Margaritella globosa.
Baculites chicoensis.
Inoceramus vancouverensis.
Axinæa veatchi.

Although this list contains several species found in the Shasta Group the predominating character is that of the Upper Cretaceous.

At the northeastern extremity of the point, and about a mile west of Old San Diego, is a bluff consisting of sandstone and some shale carrying casts of Eocene fossils. Quite a variety was found here but specific determinations were in many cases impossible so that the list is not given. The strata dip northeasterly at a small angle and though they cannot be traced by surface outcrops the whole of the distance to the Chico beds at the southern end of the point four miles away, yet judging from the scattered exposures with the same character and similar dip, the indications are that they are conformable with the Chico. The vertical distance between the two fossiliferous beds is probably not over twelve hundred feet. It would appear that the Chico and Tejon are conformable here as in many other parts of the State, but that there is no blending of the faunas of the two divisions.

The Miocene is not positively recognized near San Diego, but the mesas along the eastern side of the bay on which the city is situated are filled with Pliocene fossils; the strata being separated from the Chico-Tejon by a small non-conformity.

As has been mentioned before, the rocks dip south on the north side of False Bay. The angle is small but quite uniform until La Jolla is reached when for a short distance it becomes much greater, then just north of the town where a shallow bay indents the land, there is quite an abrupt reversal of the dip toward the northeast, the angle being as much as 30 degrees. The northern side of this anticlinal is exposed along the shore for a half a mile. The rock is chiefly shale with some heavy bedded sandstones, and contains a fauna somewhat similar to that on Point Loma save that it is not as varied. The following species were determined.

Hamites vancouverensis.
Helcion dichotoma.
Inoceramus vancouverensis.
Megertia?
Mytilus pauperculus.
Pecten —— n. s.
Stomatia —— n. s.
Ammonites hoffmani.
Axinaea veatchi.
Chione varians.
Cinulia obliqua.
Gryphæa vesicularis.
Pecten traski.
Terebratula —— n. s.
Septifer dichotomus.
Solen parallelus.
Coralliochama orcutti.
Baclites chicoensis.

At both Pt. Loma and La Jolla the fossiliferous Cretaceous strata appear only at the highest point in the anticlinal.

A little valley opens out to ocean north of the Cretaceous strata just described and no outcrops appear for nearly a mile. North of the valley there begins a long stretch of perpendicular cliffs rising nearly four hundred feet. The strata have the same dip and strike as those forming the northern side of the anticlinal at La Jolla. At the base are a few Eocene fossils which become more abundant northward along the coast, that is higher in the series. No contact of the Eocene with the Chico is shown but there is apparently a conformability.

The conclusion to be drawn from these facts warrants the assumption that the Coralliochama is a distinctly Chico fossil in the three known localities on the southern coast, namely:— Todos Santos bay, Pt. Loma and La Jolla, and though there are no stratigraphical relations shown near Wallala, yet the general character of the beds and the resemblance of the fauna to that of the localities just described, leads me to the belief that they are all approximately synchronous. It will be seen on comparison of the list of fossils that about half of those from Todos Santos were found at Pt. Loma and La Jolla, while

the strata at the two latter localities were seen to be followed upwards in a short distance by well characterized Eocene.

Richly fossiliferous beds of the Upper Cretaceous lie along the western slope of the Santa Ana Mountains, about one hundred miles north of San Diego. The fauna is, however, quite different from that of the localities just described, but few species being common. Westward toward the ocean the Cretaceous is followed by the Miocene without any apparent physical break. Eocene fossils have not yet been found in this region. Southward toward San Diego the Miocene is replaced by the Eocene but the boundaries have not been made out.

The Cretaceous bordering the Santa Ana Mountains dips away at a high angle, and shows a basal conglomerate resting unconformably on the somewhat metomorphosed Paleozoic Series.

The Lower Cretaceous has not yet been recognized in southern California, unless it be in some local beds on the summit of the Carrizo Mts., on the western border of the Colorado Desert. The locality is about seventy miles east of San Diego and on the opposite side of the Peninsula Range. Fossils are numerous but in poor condition, save for one species of the coral Astræa which is in large masses and exceedingly well preserved. The beds are unconformable with the Miocene and very much older. The region is a very interesting one and deserves careful study.

The discoveries announced in the foregoing article add emphasis to the fact that too much care cannot be exercised in classifying beds when only a scanty paleontological evidence is available. The importance of stratigraphy and lithology has been greatly undervalued in the study of California geology. In my opinion it is one of the reasons that such serious mistakes have been made in the classification of the older rocks of the Coast Ranges.

ART. LVII.—*On the Nature of Certain Solutions and on a New Means of investigating them;* by M. CAREY LEA.

[Read before the National Academy, April, 1893, by Dr. George F. Barker.]

THE three strong acids with which we are best acquainted have this in common that they all form two classes of compounds, the one perfectly neutral and perfectly stable in solution, the other class instantly decomposing when it is attempted to dissolve them in water. As types of the first class may be taken the alkaline salts. Of the second, mercuric sulphate,

bismuth nitrate and stannous chloride offer examples, as also the thallic salts of all three.

Between these limiting cases are certain intermediate ones as to which our knowledge of the form which the salts take in solution is not very exact.—It need scarcely be mentioned that what has been said does not refer to dissociation into anions and kations but into separation of free acid and basic salt, an entirely different question.

In the case of sulphates—to a consideration of which this paper will be devoted—we know that the number of salts of the metals which give a purely neutral reaction with litmus is comparatively small; that all the normal sulphates of the heavy metals show an acid reaction even after any number of recrystallizations although these may be made from solutions rendered alkaline by the addition of free alkali, and that all the normal sesquisulphates have an acid reaction. The question is as to the meaning of this acid reaction and whether in any or all cases free acid is present.

The uncertainty that exists depends partly upon the imperfect nature of our indicators. Litmus, which is perhaps the best, is reddened by the contact of any substance which will deprive it of its alkali. Methyl orange, which is by some considered more sensitive than litmus, has this disadvantage that it seems to be decomposed by some metallic salts so that its color is rendered lighter by them instead of darker although free acid may be present. This tendency greatly diminishes its usefulness.

Another method has been proposed for the detection of free sulphuric acid in the presence of combined. The solution is heated to 100° and evaporated to dryness in the presence of a small quantity of organic matter which is blackened if free sulphuric acid is present. As what we want is to determine the nature of the *solution* at ordinary temperatures such a method is quite worthless.

But by means of a new reaction the conditions of such solutions can be examined and free sulphuric acid can be detected in the presence of sulphates with great accuracy and sharpness even when only a trace is present.

The method is as follows: Taking the well known polarizing salt discovered by Herapath, the sulphate of iodo-quinia, it is possible to remove the whole of the sulphuric acid without breaking up the molecule. This may be done with either barium carbonate or barium hydroxide. The mode of operation is as follows. The barium compound is placed in a beaker and covered with weak alcohol of about 70 per cent. Into this the crystallized herapathite is dropped. In cold alcohol of this strength it is but very slightly soluble but in the presence of the barium compound it dissolves with facility and in large

quantity forming a deep sherry wine-colored liquid. This solution when allowed to dry spontaneously leaves an amber-colored varnish without a trace of crystallization. If, however, we add to this solution a minute quantity of sulphuric acid there is left behind on evaporating a characteristic bluish black film and isolated crystals of iodo-quinia sulphate. In forming this reagent it is more convenient to employ barium carbonate as the decomposition is effected equally well and with it we are certain that the solution contains no barium compound. Barium carbonate decomposes iodo-quinia sulphate with slow disengagement of carbonic anhydride, it seems therefore probable that the resulting solution contains a free base.

From this solution the sulphate is regenerated with great facility by free, but not by combined sulphuric acid. And as the herapathite thus formed is a well characterized substance we obtain a most useful means of deciding as to whether sulphuric acid in certain solutions is free or combined. It is not necessary that the combined sulphuric acid should be united to a strong base, neutral sulphates of weak bases are wholly without action. Thus neither brucia nor quinia sulphate causes formation of herapathite, the sulphuric acid in these salts has no more tendency to bring about the reaction than for example that in sodium sulphate. The fact that quinia sulphate does not form herapathite with the test, indicates that there is *no* free iodine present, thus confirming the view that the iodoquinia molecule is not broken up.

Space cannot be spared here to go with detail into the chemistry of iodoquinia compounds. The whole series of acid persulphates has been most thoroughly studied by Jörgensen* who distinguishes seven compounds of quinia, sulphuric acid, and iodine of which four belong to the herapathite type, that is, they contain three molecules of sulphuric acid to four of quinia, and two of hydriodic acid, with increasing amounts of iodine. Putting Ch for $C_{20}H_{24}N_2O_2$, the composition of these four salts may be taken as

$$4Ch,\ 3H_2SO_4,\ 2HI,\ I_4$$
$$4Ch,\ 3H_2SO_4,\ 2HI,\ I_5$$
$$4Ch,\ 3H_2SO_4,\ 2HI,\ I_6$$
$$4Ch,\ 3H_2SO_4,\ 2HI,\ I_7$$

The first of which series is herapathite. All are isomorphous (l. c. p. 253). Jörgensen's view of the constitution of herapathite is that it is "half superiodide, half sulphate" he gives as its rational formula :

* Journal für praktische Chem., II, xiv, 213 ff.

$$J_2J\,.\,HChH\,.\,O\,.\,SO_2O\,.\,HChH\,.\,O\,.\,So_2O\,.\,HChH\,.\,O\,.\,SO_2\,.\,O\,.\,HChH\,.\,JJ_2\,.$$

It appears, however, that the sulphuric acid may be removed not only by barium carbonate but by its hydrate, without breaking up the molecule. It is easily shown that the solution of herapathite after treatment even with barium carbonate contains no sulphuric acid. This may be proved by adding to the solution after the treatment, ammonia till it becomes pale yellow, evaporating to dryness and then warming with very dilute hydrochloric acid. An aqueous solution of barium chloride then gives no precipitate, nor even any troubling by standing. It seems perhaps doubtful if a substance having the constitution indicated by the rational formula above cited could have its molecule subsist unbroken, after the removal of the sulphuric acid.

The application of this test leads to the following conclusions:

1. *Sulphates of the type* R'_2SO_4 *or* $R''SO_4$

I find that these salts dissolve in water and exist in solution as such and absolutely without separation of sulphuric acid even in those cases in which the solution is acid to litmus. The substances examined were the alkaline sulphates and the sulphates of Mg, Zn, Cd, Cu, Ni, Co, Mn, Tl, also the sulphates of morphia, quinia, strychnia and brucia. To this series of reactions there is a single exception of an interesting character.

A solution of ferrous sulphate invariably contains free acid, no matter how often recrystallized or under what circumstances prepared. A small flask was filled with freshly distilled water and was well boiled, corked and set aside to cool. In this, ferrous sulphate was dissolved and potash was added in quantity sufficient to precipitate a considerable proportion of oxide. Even this solution gave the reaction indicating the presence of free acid. So too the double salts of ferrous oxide with ammonia and with magnesia, their solutions always contain free acid, no matter how often they may be recrystallized or purified by precipitation of their solutions in water by alcohol. This exceptional behavior probably results from the great tendency of ferrous solutions to rapid absorption of oxygen from the air, and as will presently appear, sesquisulphates are dissociated in solution.

With this one exception the heavy metallic sulphates above mentioned dissolve in water without decomposition although their solutions redden litmus. The alkaloids mentioned yield sulphates which after suitable purification are perfectly neutral to litmus.

To explain this contrast it is necessary to remember that a salt reddens litmus whenever the affinity of its acid for the potash in litmus is not held in check by two affinities which oppose it, that of the base for its acid and that of the litmus dye for its potash. If the base is sufficiently weak, the affinity of its acid for potash preponderates.* The whole question therefore reduces itself to that of the strength of the base with which the acid is united, and it consequently follows irresistibly that even very weak alkaloids are stronger bases than such metallic oxides as those of zinc, copper, cobalt, etc.

Although this deduction seems clear it may be supported by additional evidence. As bases, the alkaloids vary very greatly in strength. A few which contain no oxygen are bases approximating to ammonia in strength. Such are nicotia and conia. Among those which contain oxygen there is much difference in strength, morphia and codeia are strong bases and are known to precipitate iron, copper, cobalt and nickel salts. The weaker alkaloids do not seem to have been examined in this respect and one therefore was selected for examination.

Brucia is one of the weaker alkaloids. It is precipitated from its saline solutions by morphia, strychnia, etc. It forms a neutral and an acid sulphate both crystallizing well. The alkaloid itself is very sparingly soluble in cold water, it is therefore convenient to operate with solutions raised to a temperature of 50° or 60° C. The sulphates of zinc, cadmium, copper, manganese, nickel and cobalt, proved to be readily precipitated by brucia. The reaction is always easily obtained and well marked. It is particularly so in the case of cobalt, the rose red solution of which becomes quickly filled with blue flocks of oxide.

That weak bases such as the oxides of zinc, cadmium, and copper should be precipitated by a weak alkaloid like brucia is not surprising but the case is somewhat different with stronger bases like manganous oxide and the oxides of nickel and cobalt. These two last are classed by Mendeléef as "fairly energetic" bases. This, however, can be understood only by comparison; no base can be considered as a strong one whose neutral salts redden litmus.

When brucia is added to solution of magnesium sulphate there is no precipitation. Magnesia is a stronger base and its salts are neutral to litmus not because the acids are more fully saturated by it but because the potash of the litmus is unable to detach the acids from the base.

*It is of interest to observe that the reaction may be changed by the presence of an additional substance although the latter may be quite neutral. Thus mercuric chloride is faintly acid to litmus, but not after the addition of potassium chloride. The tendency to form a double salt changes the balance of affinities.

2. *Sesquisulphates.*

Chromic sulphate.—The violet salt was obtained free from green salt by acting on the nitrate with sulphuric acid. It was freed from excess of acid by repeated precipitation with alcohol and thorough washing. It had a pale violet color and satiny luster. In solution it always gave when examined with the test liquid, marked indications of the presence of free sulphuric acid.

Aluminum sulphate.—This was purified from excess of acid in the same manner as the preceding and gave a similar reaction.

Glucinum sulphate.—Same treatment as the preceding and similar reaction.

Ferric sulphate.—Same reaction.

In all these cases the reaction was extremely well marked. It indicates that these sulphates do not exist as such in solution but that a portion of their acid is set free.

3. *Alums.*

The alums as might be expected show reactions similar to those of the sesquisulphates with one notable exception.

Potash alumina alum is always dissociated in solution. A specimen made by combining pure aluminum sulphate with potassium sulphate was recrystallized ten times with thorough washing of the crystals. The presence of free sulphuric acid was as evident after the last recrystallization as before.

Ammonia ferric alum is also dissociated by solution.

Potash chrome alum.—This alum differs remarkably from the others. After two or three recrystallizations which of course must be made at low temperatures, the crystals may be dissolved in water without dissociation. The test liquid indicates that there is no free sulphuric acid present.

It appears therefore that this alum alone of its congeners exists as an alum in solution.

The alums consequently form a series with varying properties, according to the nature of the sesquisalt present. At the head stands chrome alum perfectly stable in solution; next alumina alum dissociated in solution but reforming itself by crystallization with the utmost facility; next ferric alum also dissociated and also reforming itself by crystallization but with less facility. And finally manganese alum whose violet octahedra are so completely dissociated by solution in pure water that they cannot be reproduced by crystallization.

4. *Acid Sulphates.*

At one time it was considered to be an established fact that the acid salts of the alkaline bases were completely decomposed by solution in water into neutral salt and free acid. In a review of this subject Berthelot quotes Andrews, and Favre and Silbermann as expressing this opinion positively and without question.* His own investigation led him to the conclusion that the separation was never complete, that a certain proportion of acid sulphate was always present, diminishing in proportion to the amount of water present; increasing in proportion to the amount of free acid. The formation of acid sulphate was always endothermic, was accompanied by the absorption of 1·05 cal. in the case of $NaHSO_4$.† He especially remarks that when a very small proportion of acid is added the tendency is to a complete combination in the form of acid salt.

This last mentioned result is contrary to that which I have been able to observe and I will therefore mention my reactions with some particularity.

I invariably found that when a trace of sulphuric acid was added to the solution of a neutral alkaline sulphate it reacted as free acid. The matter was examined especially in the following manner. To 40^{cc} of distilled water 2 drops of sulphuric acid were added, the liquid was divided into two equal parts in one of which was dissolved a gram of neutral sodium sulphate. These two liquids were then examined with the test solution and the detection of the acid was found to be fully as easy in the presence of the large excess of sodium sulphate as in the case of the acid alone.

It is true that this result is open to the following criticism. Alcohol extracts sulphuric acid from solid acid sodium sulphate showing thereby, as Mendeléef remarks, the extremely weak affinity which unites it to the neutral salt. In the present examination the test can only be used in alcoholic solution. It may be said that the alcohol first precipitates the solid acid sulphate and then abstracts free acid from it. There is force in this objection but I think it may be answered in the following manner. We first reduce sulphuric acid nearly to the limit of dilution and quantity at which it can be detected. We then find that the addition of a comparatively large quantity of neutral sulphate makes absolutely no change in the reaction. It seems therefore legitimate to conclude that no combination has taken place because otherwise it would be necessary to admit that alcohol can abstract all the acid united with the solid neutral sulphate, which is highly improbable.

* Mech. Chim., ii, 318. † Mech. Ch., ii, 323.

The weight of the evidence seems therefore to favor complete decomposition by solution into neutral salt and free acid.

When herapathite is dehydrated either by long keeping over oil of vitriol, or by exposure to a temperature of 100° C. for several hours its color changes from green to dark brown and its luster is lost. In this condition it dissolves sparingly in boiling absolute alcohol and separates by cooling in blackish particles which show little trace of crystallization.

When the brown substance is placed in a vial with barium carbonate also dried, and absolute alcohol, scarcely a trace of action ensues. The liquid, even if kept warm, scarcely colors and the brown color of the salt is retained. The addition of a little water brings on rapid action. The dull brown color changes to bright metallic green and solution goes on steadily as the sulphuric acid is removed by the barium carbonate.

We thus have the curious result that two substances, both entirely insoluble in water, scarcely act on each other until water is present, and then a rapid decomposition results.

The question naturally presents itself whether it is necessary to first form and then decompose herapathite or whether a suitable test solution could not be obtained by simply acting on quinia with iodine. An iodine solution instantly produces in one of quinia a bulky precipitate of a light yellowish brown color, quickly redissolving if the solutions were not too strong and the liquid thus obtained if the iodine is not in excess, immediately forms herapathite on the addition of sulphuric acid.

But the reaction is not a delicate one; a trace of sulphuric acid cannot be detected as with the solution obtained from herapathite. The reason appears to be as follows: When pure herapathite is used the resulting solution contains absolutely no excess of either quinia or iodine. But, however carefully we may attempt to mix quinia and iodine we will always have a slight excess of one or the other and in either case the delicacy of its reaction is lost. If quinia is present in excess a trace of sulphuric acid is required to saturate it and it has been already mentioned that the test solution will not take sulphuric acid from quinia or from any other alkaloid. On the other hand, if iodine is present in excess the first action is to form one of the more highly iodised bases, more soluble than herapathite and crystallizing less well. So that in either case a trace of sulphuric acid is consumed before the proper reaction occurs and if only a trace is present the reaction may fail.

It is better therefore to prepare herapathite in the first place and a convenient means of obtaining it will be here given.

In a Griffin's beaker place 100^{cc} of alcohol of 95 per cent add 5 grams of quinia sulphate and 40^{cc} of acetic acid of 50 per cent. Take dilute sulphuric acid containing one-tenth by weight of acid and add of this 7^{cc}. Place the beaker in a water bath and apply heat till the alcohol begins to boil gently, then add with constant stirring 20^{cc} of a ten per cent solution of iodine. Turn off the heat, cover the beaker with a glass plate and allow it to cool slowly with the bath. Next day throw the crystals on a filter and wash with 70 per cent alcohol. Press between blotting paper and dry at ordinary temperature.

Herapathite appears to be a very permanent substance. Some that I prepared over thirty years ago has been kept in a stoppered but not sealed white glass bottle and freely exposed to light during this time. It appears to be quite unchanged and was used in part of the work just described.

In preparing the test solution time is gained by using the barium carbonate in considerable excess and by frequent shaking. The herapathite should be in fine powder. After the green particles have entirely disappeared, which will usually take a day or two, the solution must be filtered off and be placed in contact with a fresh portion of barium carbonate with frequent shaking for several days. The complete removal of the last traces of sulphuric acid cannot be judged of, as might be supposed, by allowing a portion to evaporate and examining for the crystals of herapathite. A specimen may dry up to a yellow varnish and yet may contain sulphuric acid as may be shown by evaporating to dryness with a little ammonia, exhausting the residue with very dilute hydrochloric acid and adding a drop of barium chloride solution. But there is a very much simpler and at the same time more effective means of testing. A solution is allowed to evaporate spontaneously after adding a drop or two of solution of oxalic acid. Then if there is the slightest trace of herapathite present it will show itself in extremely characteristic crystals, either small rosettes of black prisms or in thin light brown transparent plates which are black when crossed. A great many acids have this property of forcing out a crystallization, for example acetic, citric, tartaric, malic and even arsenic. On the other hand hydrochloric, hydrobromic and nitric acids have not this power.

The explanation appears to be this. Iodoquinia is a colloid and when present in large excess is able to prevent the crystallization of the relatively small proportion of herapathite present. The addition of either of the first named series of acids appears to convert the colloid base into a crystalline salt

which of course no longer interferes with the crystallization of the herapathite.

Method of applying the test.—After having ascertained in the above mentioned manner that the test solution is absolutely free from herapathite, a few drops of the liquid to be tested are to be placed in a small porcelain basin, a little alcohol added and then a few drops of test solution. When the quantity of sulphuric acid is something more than a trace an immediate black precipitate is formed. If the quantity is something less, no immediate result is visible but as the alcohol evaporates, it leaves behind a film of dark crystals which under a lens are easily recognizable. In this way a quantity of sulphuric acid amounting only to ·000015 gram, about $\frac{1}{66}$ of a milligram, can be detected with certainty provided the test solution is not used in too great excess. To detect so small a quantity however requires some familiarity with the reaction.

With larger quantities of free sulphuric acid the characteristic violet-black crystalline precipitate falls immediately. In dealing with quantities too small to cause precipitation it is advantageous to gently warm the basin beforehand; in this way a crystallization is obtained within two or three minutes and the danger of secondary reactions such as might be caused by the presence of oxidizing acids is diminished.*

The conclusions derived from the foregoing investigations may be briefly summed up as follows:—

1. The solution of iodoquinia affords the means of detecting free sulphuric acid even in traces in presence of combined sulphuric acid.
2. The salts of heavy metallic protoxides do not owe their acid reaction to dissociation. The solutions of their sulphates contain no free sulphuric acid. To this there is one exception. Solutions of ferrous sulphate always contain free sulphuric acid.
3. Sesquisulphates as far as examined are always dissociated in solution.
4. Alums are always dissociated in solution with a single notable exception. Chrome alum exists as such in solution.
5. Acid salts are dissociated in solution. The dissociation is very great and may perhaps be complete.

Philad., April, 1893.

*Very faint traces of free sulphuric acid are detected as follows: If the test liquid dries up without showing indications, 1 or 2^{cc} of alcohol are poured into the basin and slowly washed round. As the yellow film dissolves it may leave behind it a violet black film of herapathite which being much less soluble resists the action of the alcohol longer. This is a test of very great delicacy and the treatment with alcohol should never be omitted.

ART. LVIII.—*Mineralogical Notes;* by ALFRED J. MOSES.

1. *Pyrite Crystals from Kings Bridge, N. Y.*

THE crystals described in this paper were obtained on November 19, 1892, by G. F. Sherman and E. H. Messiter, students of the Columbia College School of Mines, from material recently quarried within 300 feet of the eastern end of the cut known as "the Harlem River Improvement" at Kings Bridge, New York City. The pyrite crystals were in a narrow cavity, in a block of limestone, associated with small crystals of dolomite, very pretty crystals of pale green transparent mica and curiously modified crystals of quartz. In a few instances minute crystals of rutile were also noticed.

The pyrite crystals are rarely more than $\frac{1}{4}$ inch in their longest dimension but a few were found almost $\frac{1}{2}$ inch in length. In most of the crystals the prevailing form is the octahedron always however modified by three or more other forms. The curious fact was noticed that in all the specimens showing quartz the general shape of the pyrite crystals was cubic and the crystals were relatively small. No large crystals of the cubic type were observed.

The angles were measured with a Mallard-Wollaston goniometer reading to half minutes. The angles obtained were:

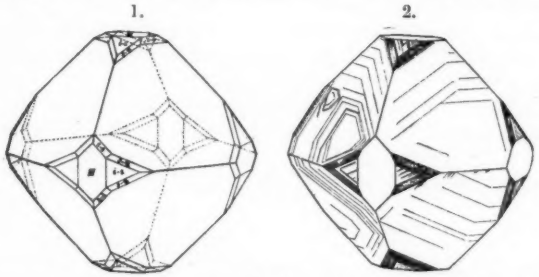
	Measured.	Calculated.
$1 \wedge i\text{–}2$	39° 13½′	39° 16′
$1 \wedge 3\text{–}\frac{3}{2}$	22° 14½′	22° 15′
$1 \wedge 2\text{–}2$	19° 25½′	19° 28′
$\mathrm{H} \wedge 2\text{–}2$	35° 19′	35° 16′
$i\text{–}2 \wedge 3\text{–}\frac{3}{2}$	16° 59′	17° 1½′

Closer results might have been obtained by readjustment but these were sufficiently exact to determine the symbols beyond question.

The occurring faces (see fig. 1) are therefore the common faces of pyrite: cube (100, i–i); octahedron (111, 1); and pentagonal dodecahedron (120, i–2); and the rarer forms: diploid (321, 3–$\frac{3}{2}$) and tetragonal trisoctahedron (211, 2–2).

In pyrite crystals striations are frequently found upon the faces of the cube and pyritohedron (i–2) parallel to the intersections of the faces of these forms and this is attributed to oscillations between the two forms. In the crystals from Kings Bridge all faces *except* those of the cube are more or less striated sometimes with only one or two very prominent lines, at other times in several directions and with many lines.

The accompanying figure (2) copies striations observed upon two crystals; the upper left hand octahedral face in particular is a fairly accurate reproduction. The striations on octahedral faces rarely if ever cross and in each face are parallel always



either to its intersections with the cube or with the pyritohedron *i*–2. The striations on the diploid and the pyritohedron were not parallel to intersections with the cube but to intersections with each other (or with the octahedron). No striations were observed on any cube face.

2. *Ettringite from Tombstone, Arizona, and a formula for Ettringite.*

The first specimen of this mineral I received over a year ago and proved it to be a hydrated sulphate of alumina and lime, but was prevented from making a complete examination by the small amount of material available. Since that time I have received and examined several other specimens.

The mineral was found by Mr. W. F. Staunton in an ore shoot in the white crystalline limestone of the Lucky-Cuss Mine, Tombstone, Arizona; just at the water level. It occurs incrusting a massive silicate of lime and alumina from which it has apparently been produced by the action of sulphuric acid, as it frequently fills little veins and hollows in the silicate and the latter is usually in these portions loosely coherent as if corroded.

In appearance the sulphate resembles a fibrous pectolite as it is made up of white somewhat translucent radiating fibers of a length up to one inch, or sometimes in little bunches of silky parallel fibers. No crystals have been found but the fibers are doubly refracting and appear to extinguish parallel to their length; cross fractures (or cleavage) approximately at right angles to the length are frequent. The hardness is a little over 2 and the specific gravity determined on 200^{mg} was 1·55.*

* If the silicate in the sample is assumed to be of the specific gravity of the silicate gangue (2 66) the gravity of the sulphate is reduced to 1·27, but the silicate near the sulphate is very much altered and probably nearer the gravity of the sulphate.

Before the blowpipe the mineral fuses readily coloring the flame red and forming a white enamel. On grinding it is damp and adhesive. Dissolves partially in water to an alkaline solution and is rapidly and completely decomposed by hydrochloric or even acetic acid.

It differs from the ettringite of Prof. Lehmann in that the latter occurs in needle-like hexagonal crystals, has a recorded specific gravity of 1·75 and is said to be infusible.

From the tendency of the portions of the silicate nearest the sulphate to crumble the material for analysis had to be picked almost fiber by fiber. Upon the purest sample thus obtained a complete analysis yielded:

	No. I. On ·2235 grms.
CaO	25·615
Al_2O_3	10·157
SO_3	17·675
H_2O (at 115°)	33·109
Loss (at red heat)	10·872
SiO_2	1·901
	99·329

The SiO_2 is present as a silicate more or less impregnated with metallic ores but which two analyses show to contain proportionately SiO_2 100 pts., CaO 27·89 pts., Al_2O_3 47·02 pts., H_2O (at 115°) 9·70 pts., H_2O (at red heat) 25·97 pts. Deducting in this proportion and recalculating to 100 we have:

	No. I (recalculated).
CaO	26·31
Al_2O_3	9·72
SO_3	18·54
H_2O (115°)	34·53
H_2O (red heat)	10·88

To prove that there had been no volatilization of SO_3 or reduction to sulphide during ignition ·2088 gms. of the mineral was dissolved in acid without ignition and the SO_3 and SiO_2 determined.

SO_3	15·066
SiO_2	9·909

Recalculated as in previous analysis this corresponded to SO_3 19·03.

An attempt was made to obtain another complete analysis on a sample of material not quite so pure as the first but in the ignition there was a loss of SO_3 due partly to reduction to

sulphide as evidenced by effervescence and odor in the subsequent solution, and also made evident by the very low result for SO_3. The comparison therefore fails for SO_3 and ignition. The other results were:

CaO	24·174
Al_2O_3	8·298
H_2O (110°)	30·613
H_2O (ignit.)	15·514
SiO_2	3·497

Recalculated as in No. 1 these correspond to

CaO	25·04
Al_2O_3	7·18
H_2O (115°)	32·68
H_2O (red heat)	15·76

Another determination yielded CaO 23·445, SiO_2 3·920. Recalculating as before we find CaO 25·55.

The comparison therefore is

	Arizona mineral				Ettringite of Ettringen.
	No. I.	No. II.	No. III.	No. IV.	
CaO	26·31	25·04		25·55	27·27
Al_2O_3	9·72	7·18			7·76
SO_3	18·54		19·03		16·64
H_2O (115°)	34·53	32 68			} 45·82
H_2O (red heat)	10·88	15·76			
				Loss	2·51

If the loss in Prof. Lehmann's analysis is taken as SO_3 the comparison is still more striking and my own results in No. II proved the probability of such a loss.

Analysis No. I of the Arizona mineral was very satisfactory in all respects, needed very slight deductions and recalculations and I prefer to regard the other determinations as confirmatory but not worthy to be averaged with this of No. I. The formula suggested for ettringite was $6CaO, Al_2O_3, 3SO_3, 33H_2O$; but the analysis of No. I suggests a more simple formula very closely fitting the analysis.

	No. I.		Approximate ratio.
CaO	26·31 ÷ 56	·470	10
Al_2O_3	9·72 ÷ 102	·095	2
SO_3	18·54 ÷ 80	·232	5
H_2O (115°)	34·53 ÷ 18	1·918	40
H_2O (red heat)	10·88 ÷ 18	·605	14

This means a mineral of closely the type of felsöbányite ($2Al_2O_3 . SO_3 + 10H_2O$), for the ratio yields $(H_{28}Ca_{10}Al_4)O_{30}(SO_3)_5 + 40H_2O$ or $2R_2O_3 . SO_3 + 8H_2O$. This formula not only suits the analysis of the Arizona mineral almost exactly but that of the Ettringen variety at least as well as the formula assumed as may be seen.

	Ettringite of Ettringen.	Ettringite of Arizona.	Percentages required by $(H_{28}Ca_{10}Al_4)O_{30}$ $(SO_3)_5 + 40H_2O$.	Percentages required by $6CaO, Al_2O_3, 3SO_3$ $32H_2O$.
CaO	27·27	26·31	26·21	26·4
Al_2O_3	7·76	9·72	9·55	8·0
SO_3	19·15	18·54	18·72	18·9
H_2O	45·82	45·41	45·50	46·7

We may therefore conclude that this mineral is to be placed in a group of hydrous basic sulphates of the general formula $2R_2O_3 . SO_3 + nH_2O$ and that the definite and close division between the loss at 115° and at red heat in my analysis supports the supposition that 14 pts. of H_2O may be considered as basic in the Arizona variety while the almost perfect agreement in total H_2O in the Arizona and Ettringen analyses makes a similar assertion for the latter not improbable.

The calculated ratio would yield the formula for the Arizona variety

$$H_{28}Ca_{10}Al_4O_{30} . 5SO_3 + 40H_2O$$

While the assumed formula for the Ettringen variety might be written

$$H_{18}Ca_6Al_2O_{18} . 3SO_3 + 24H_2O$$

Both of these are of the type $2R_2O_3 . SO_3 + nH_2O$ and closely agree when reduced

Arizona variety .... $2[H_{\frac{14}{5}}CaAl_{\frac{2}{5}}O_3] . SO_3 + 8H_2O$

Ettringen variety . $2[H_3CaAl_{\frac{1}{3}}O_3] . SO_3 + 8H_2O$

The group therefore of hydrous basic sulphates of the general formula $2R_2O_3 . SO_3 + nH_2O$ is composed of

Glockerite	$2Fe_2O_3 . SO_3 + 6H_2O$	Earthy or massive.	
Felsöbányite	$2Al_2O_3 . SO_3 + 10H_2O$	Orthorhombic six sided scales.	
Paraluminite	$2Al_2O_3 . SO_3 + 15H_2O$	Massive.	
Ettringite	Arizona . $2[H_{\frac{14}{5}}CaAl_{\frac{2}{5}}O_3].SO_3 + 8H_2O$	Silky double refracting fibers.	
	Ettringen $2[H_3CaAl_{\frac{1}{3}}O_3] . SO_3 + 8H_2O$	Hexagonal needle crystals.	

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ART. LVIX.—*On Pentlandite from Sudbury, Ontario, Canada, with Remarks upon three supposed new species from the same Region;* by S. L. PENFIELD.

Pentlandite.

UP to the present time the occurrence of pentlandite at the Sudbury nickel and copper mines has never, to the author's knowledge, been definitely proved. Some years ago Mr. F. L. Sperry, then chemist of the Canadian Copper Company, sent a suite of Sudbury ores to the Sheffield Scientific School and several of these were carefully analyzed by Mr. J. F. McKenzie, a student at the time in the Sheffield Laboratory. His results have been published only as a private contribution in the sixth edition of Dana's Mineralogy. Analysis 17, page 74, is of a nickeliferous pyrrhotite, with Fe = 56·39 and Ni = 4·66 per cent. Analysis 3, page 65, is of a normal sulphide of iron and nickel, with Fe = 25·81 and Ni = 39·85 per cent, the latter including a trace of cobalt. The specimen from which the material for the latter analysis was taken was a piece of massive ore, apparently very pure. The writer examined it carefully for indications of isometric crystallization or octahedral cleavage, but none could be found; it seemed to break everywhere with irregular fracture. The specimen was referred, however, to the isometric pentlandite because it agreed better in its chemical composition with that species than with pyrrhotite.

Later, among the same lot of specimens sent by Mr. Sperry, a piece was found composed mostly of massive pyrrhotite but showing in places a mineral lighter in color and which broke with flat surfaces. On separating some of the latter it was found to differ from pyrrhotite in being non-magnetic and giving a strong reaction for nickel before the blowpipe. Moreover on a number of pieces the angle between the flat surfaces was measured twelve different times on the reflecting goniometer within the limits 70° 23′ and 70° 46′, giving as a mean 70° 33′, which agrees well with the angle of the isometric octahedron 70° 32′. Three of the above angles were measured in different zones on a single fragment. There is no doubt, therefore, but that the mineral in question is isometric. The flat surfaces are apparently not the result of an octahedral cleavage but rather planes of parting, of secondary origin, similar to the octahedral parting observed on some varieties of magnetite.* The fracture of the mineral is irregular and the

*A. Cathrein, Zeitschr. Kryst., xii, p. 47, 1886. O. Müggs, Jahrb. Min., i, p. 244, 1889. J. F. Kemp. This Journal, xl, p. 62, 1890.

distinct parting was observed only at certain intervals. The attempt to cleave from a given piece an octahedron was not successful and among a great many fragments which were examined only one was found with a distinct octahedral shape. This octahedral parting, rather than cleavage, is perhaps characteristic of the pentlandite from the original locality in Lillehammer, southern Norway. Scheerer in his original article* describes it as follows: "Molecular structure: Foliated parallel to the faces of a regular octahedron. Fracture: in places which show no foliation, fine-grained to conchoidal."†

As the associated pyrrhotite was strongly magnetic the separation of the two minerals could readily be made. The ore was crushed and sifted to a grain of from $1-2^{mm}$ in diameter and the pyrrhotite was extracted by means of an ordinary magnet. The pentlandite for analysis was further carefully selected by hand picking. The specific gravity of this portion was found to be 5·006. This was so much higher than that given by Scheerer, 4·60, that a second sample was separated which gave 4·946. The pure mineral had a pale yellowish bronze color, between that of pyrite and pyrrhotite. The analysis is as follows:

		Ratio.	
S	33·42	1·044	
Fe	30·25	·451	1·047
Ni	34·23	·582	
Co	·85	·014	
Gangue	·67		
	99·42		

The gangue was silica which had undoubtedly separated from some decomposable silicate, but no attempt was made to determine the small amount of bases in combination with it. The ratio of S : (Fe + Ni) is 1·044 : 1·047, almost exactly 1 : 1 or that of a normal sulphide. The ratio of Fe : Ni is 1 : 1·32 while in pentlandite from Lillehammer it is about 2 : 1.

On three supposed new Sulphides of Iron and Nickel from the Sudbury Region.

Folgerite.

In a recent number of the Journal of the American Chemical Society,‡ Dr. S. H. Emmens has described as a new species

* Pogg. Ann., lviii, p. 315, 1843.

† "Innere Form: Blätterdurch gänge parallel den Flächen eines regulären Octaëders. Bruch: auf Stellen wo sich keine Blätterdurehgänge zeigen, feinkörnig in's Muschlige."

‡ Vol. xiv, No. 7.

a sulphide from the Worthington Mine, on the Algoma Branch of the Canadian Pacific Railroad, about 30 miles southwest of Sudbury. To this mineral he has given the name folgerite. From his description and the analyses it is evident that folgerite is identical with the pentlandite just described. His discription of the physical properties agrees fairly well. "A fragment associated with adhering pyrrhotite showed a sp. gr. of 4·73" while that of pentlandite is 5·00. "Form, massive, with a platy structure. No crystals have as yet been observed." This description of the platy structure corresponds to some specimens of pentlandite which were seen at the laboratory of the late Prof. F. A. Genth, only a few weeks before his death. He was about to examine the mineral and had obtained specimens of the Sudbury ores from the Canadian Geological Survey. His material was much better than that examined by the author, in that it showed larger patches of the pentlandite in the pyrrhotite. The octahedral parting, developed especially in one direction, gave the platy structure noted by Dr. Emmens. A most remarkable statement by Dr. Emmens can not be readily understood. "Magnetism—In large fragments the mineral is non-magnetic. In minute grains it is magnetic. The finely triturated powder is non-magnetic." The formula proposed for this mineral is $NiFeS_2$, deduced from the following analyses by Mr. C. T. Mixer, in all of which the sulphur was determined by difference. One direct determination of sulphur in a fourth sample gave 34 per cent

	A	B	C	Calculated for $NiFeS_2$
Ni	35·20	31·45	29·78	32·87
Fe	33·70	31·01	26·89	31·30
S	31·10	37·54	43·33	35·83
	100·00	100·00	100·00	100·00

It is evident that the above are all analyses of pentlandite or of some mixture in which it predominates. They differ from the analyses of the pentlandite from Lillehammer chiefly in the relative proportion of iron and nickel, which, being isomorphous, may replace one another through a wide range. The agreement between the separate analyses and theory is far from satisfactory and certainly for the establishment of a new mineral species a direct determination of the important constituent, sulphur, should have been made. There is, therefore, no sufficient ground for making a new species of this mineral and it is to be hoped that folgerite will never find a place in mineralogical literature.

Blueite.

Under this name Dr. Emmens has described a massive sulphide ore, which is found in several mines of the Sudbury district, notably at the workings of the Emmens Metal Company, where it is found associated with niccolite, gersdorffite, pyrrhotite and chalcopyrite." The following are some of its properties. "Luster,—Metallic, somewhat silky. Color,—pale olive-gray, inclining to bronze. Specific gravity, 4·2. Form, Massive,—No crystals have as yet been observed. Solubility.—The mineral dissolves readily in nitric acid without separation of sulphur and yields a yellow solution.—Magnetism. —The mineral is non-magnetic."

The chemical analysis is given under A. B, is the same after deducting the insoluble and recalculating to 100 per cent. The theoretical composition, calculated for the proposed formula $Fe_{12}NiS_{26}$ is given under C.

	A	B	C
Ni	3·5	3·70	3·76
Fe	38·8	41·01	42·96
S (by difference)	52·3	55·29	53·28
Insoluble	5·4	----	----
	100·00	100·00	100·00

The reasons given for making a new species of this mineral are "the considerable percentage of nickel (a very rare element in pyrite) and the easy solubility in nitric acid without separation of sulphur." Although it must be admitted that nickel is a rare constituent in pyrite, yet nickeliferous pyrites are known, and at Sudbury in particular, where iron and nickel are so abundant, we might expect to find a mutual replacement of these elements. Moreover the analysis was made on massive material; there is no guarantee of the purity of the mineral and the sulphur was determined by difference. The character of the gangue is not stated and certainly no proof has been given that the nickel has not been derived from some impurity. That the mineral dissolves in nitric acid without the separation of sulphur can not be made a ground for separating it from pyrite, for it is an easy matter to oxidize and dissolve the latter completely, if the nitric acid is strong and relatively in large quantity compared with the amount of mineral to be dissolved.

Whartonite.

Under this name Dr. Emmens describes a sulphide from the Blezard Mine, about seven miles northeast of Sudbury. The

following are some of its properties. "Color,—Bronze-yellow. Luster,—Metallic. Form,—Cellular; the cavities being lined with minute cubic crystals and the intermediate substance being finely granular. Solubility,—The mineral is soluble in HNO_3 with separation of sulphur and a greenish yellow solution. Magnetism,—On comminution about 10 per cent of the mineral is found to be magnetic." The analyses are as follows.

A, of the mixture; B, Magnetic portion; C, non-magnetic portion; D, after deducting insoluble and ten per cent of magnetite from A and calculating to 100 per cent; E, theory for the proposed formula Fe_7NiS_{16}.

	A	B	C	D	E
Ni	5·40			6·27	6·10
Fe	42·90	66·55	40·4	41·44	40·68
S	45·00	7·00	52·6	52·29	53·22
Insoluble..	4·80			----	----
	98·10			100·00	100·00

Here it is known that the analyzed material is a mixture and even if it were proved that the Sudbury pyrite is nickeliferous, to the extent indicated by analysis D, it would not be best to make a new species, for certainly the replacement of a part of the iron by nickel is nothing but an illustration of the common law of isomorphism.

Blueite and whartonite, therefore, like folgerite cannot be recognized as distinct species. It is clear that little dependance can be placed upon chemical formulas deduced from analyses of material of such doubtful purity, especially where a chief constituent is determined by difference.

Mineralogical Laboratory,
Sheffield Scientific School, March, 1893.

ART. LX.—*Notes on the Geology of Florida: Two of the lesser but typical Phosphate Fields;** by LAWRENCE C. JOHNSON, U. S. Geological Survey.

[Presented, with the permission of the Director.]

A. The Geology of the Gainesville Sheet—or the "Land-pebble" phosphates of Eastern Alachua County.

COMMENCING with Lake Santa Fe, in the north, we find it, and Nunan Lake, to the southwest of it, both surrounded by a flat sandy country destitute of "sinks" and of rock exposures

* Before the Geological Society of America, Rochester, N. Y., Aug., 1892.

of any kind. Some distance off, however, to the westward of the former and about four miles west of Waldo, is a small exposure known as the Preston Marl, near old Fort Harlee; and seven or eight miles still farther northwestward in Bradford County, is another large sink. Both these exhibit formations of Miocene age. The small streams also, which traverse these flat woods, including Santa Fè river and several of its affluents, and Lockloosa creek rising by several small branches from the eastern end of Lake Santa Fè, have in them or in their immediate valleys, driftlike sediments, containing casts of fossils similar to those of Waldo. These flatwoods are said to have a general elevation of about 150 feet above tide water.

It is well to acknowledge here in advance, the assistance derived from the topograpical sheets of the Geological Survey.

Between Nunan Lake, and the great Alachua Sink or Lake, to the westward, are a number of exposures of clays, and phosphatic sandstones,—the latter being known as the Gainesville "Paving-rock." These may be regarded as alteration products of older Miocene beds. Fossils are rare; but traces exist of a *Venus*, a *Pecten*, and there is no scarcity of reptilian bones. Teeth of sharks and rays are quite numerous. In other parts of the region having this structure, and the *tufa*-like Gainesville Paving-rock, there are ferruginous marly sands with chalcedonized oyster shells not distinguishable from *O. Virginiana*, and there are also abundant patches of the large coral *Astrea Floridana* (or *bella*.) The contour lines of the Survey give the elevations of these deposits of the coral, and oysters and Gainesville rock at 70–100 feet.

At the great Alachua Sink, twenty feet lower than the lowest Gainesville rock of the adjoining hills, the formation is Eocene of the Vicksburg type.

For ten or twelve miles westward of this sink, and of Lake Nunan, the same relative position of the strata continues, with a constant gain to the Eocene rocks; until they reach the elevation of near 100 feet, and the Gainesville rock disappears, or becomes very thin and represented by its alternate clay. This probably signifies a small dip of the Eocene to the eastward; in which direction, it sinks under Miocene clays and marls.

The region south of Gainesville, a distance of ten miles, is one of apparent depression. Within it are contained Payne's Prairie—lately Lake Alachua*—the Kanapaha Prairie, and the Hogtown and Sugarfoot Prairies and Sinks. To the southeast of Payne's Prairie lie series of ponds and small cypress

* Alachua Lake was a *prairie*, from the oldest record, till 1878, when after great rains it became a lake of 40 sq. miles. Again in June, 1891, after a series of four dry years, it suddenly dried off. Immense numbers of fish were taken or destroyed. And now, July, 1892, after a month of heavy rains, the water is reclaiming possession of the flats

swamps by which it is connected with Orange Lake. The elevated ridges of this section are, like the Flatwoods region of Lake Nunan, Miocene. The depressions usually expose Vicksburg rocks, silicified. These outcrop in many old sinks upon Payne's Prairie and about the various ponds. None however on the hills, and none at the northern end of Orange Lake and Lockloosa Lake, its northeastern extension. The southern end of Orange Lake, and Tuscawilla Lake—separated from it by hammock ridges 100 feet high—expose Eocene rocks.

Orange Lake—like so many others which have an Eocene bottom—has a subterranean outlet. And less than a mile north of this "sink," it has within its basin, a "rise"—one of the great springs, so common in the Vicksburg formation of Florida. The lake has its overland outlet also in time of high water, through Orange Creek into Oklawaha River. Over all the foregoing region it is evident that great denudations have taken place, and that from 40 to 100 feet of Miocene marls and later sands have been removed: a history only to be understood upon the Hilgard hypothesis of an elevation of 600 feet and over, in Post-Tertiary times.

It is in the elevated region about Gainesville, the "Land-pebble" phosphates of Alachua occur. The derivation of these pebbles can hardly have been from beds of compact stone, whatever theory may obtain for other parts of the State. For several reasons:

First. The elevation assigned the pebble beds of this region is 150 feet above tide water. No known beds of compact hard rock occur above 75–100 feet.

Secondly. The pebbles are largely fossil casts or fragments of such casts; and it may well be assumed they had their origin in a fossiliferous marl, which by disintegration and removal of the calcium carbonates, left behind the less soluble phosphates. The aggregation of phosphatic matter in fossil forms contained in marls is well known. According to Dr. Eugene A. Smith, all the shell casts in Cretaceous rocks, as well as in those of Tertiary age, of Alabama and Mississippi, are phosphatic.

Third. Compact phosphate is not composed of fossils; nor are its beds especially fossiliferous; though phosphatic rock containing fossils may locally occur by metamorphosis of the original limestones upon which phosphate beds were deposited.

B. The "Plate-rock" Deposits of Eastern Marion County.

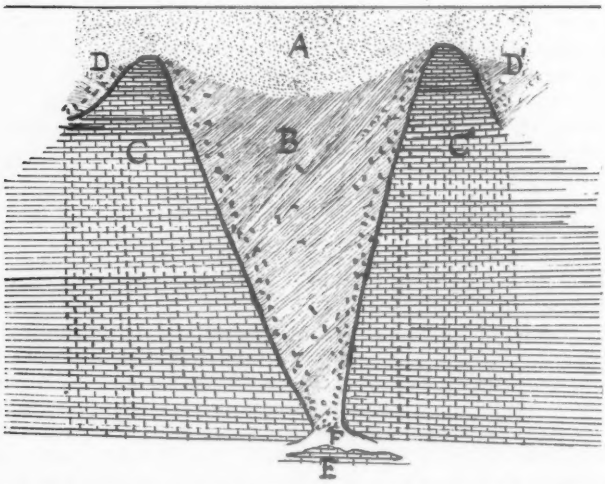
The term "plate-rock" is the mining term applied to fragmentary thin flat pieces of "Hard-rock" phosphates. It analyzes as high as any, namely: about 80 to 85 per cent tribasic calcium phosphate.

The area embracing these deposits lies some twenty miles eastward of the main belt of "hard-rock" phosphates, and extends from Citra on the southeastward bay of Orange Lake to the southwestern extension of Lake Wier, and to Wildwood in Sumter County, a distance of 40 miles, with an average width of 1½ to 3 miles.

Within this region the first mining was done by the "Peninsula Phosphate Company," near Anthony, 10 miles north of Ocala, in 1890. Other works and mines have been since undertaken at Citra, Sparr, Montague, Welshton, Belleview and Summerfield—stations on the line of the "Florida Central and Peninsular," and "Florida Southern" Railroads. In only a few of these places, however, have excavations been sufficiently extensive to afford a complete insight into the nature extent and value of the deposits, yet in the smallest *prospect* hole, some facts of value are found.

The following figure may give a fair notion of the general mode of occurrence of this class of phosphates.

1.



Excavation in progress at "The Ohio Mining Co's" works, Sparr, Fla. This mine is selected from scores examined, on account of its exceeding regularity.

A, "Overburthen"—soil and sand—8 ft. in its greatest thickness.

B, Great mass of "Soft-phosphate," and matrix of the fragments of "Plate-rock," narrowing to 2 ft. at bottom—30 feet deep.

C, C′, The two buttresses or pinnacles of Vicksburg limestone—by the miners called "Lime-horses."

C is 33 feet high, C′ 34 ft.

D, D′, Trial excavations just begun.

E, Calcite rock beneath; F, The drainage cavity.

This pit is 38 feet deep, from the top of sandy soil, to the cavity at the base. It is 28 feet across between the tops of the pinnacles, which are 2 feet apart at the base, where the cavity opens. The "plate-rock" is the thin layer next the limestone shoulder imbedded in the interior matrix of "soft-phosphate" —a little argillaceous. This

"Plate-rock" carries 79½ per cent tribasic phosphate of lime.
The soft phos. matrix " 69 " " " " "

Attention is called in this section:

(1) To the "overburthen" of surface sand which, on the tops of the pinnacles of limestone, is approximately 4 feet, while in the center it is sunken and grades to 8 feet in depth.

(2) To the filling between the pinnacles, which is chiefly "soft-phosphate," a substance of clay-like appearance and consistency, of a creamy color. It is very variable in its phosphate of lime—often high in alumina and iron. In this instance it is a 69 per cent phosphate.

(3) To the comparatively small portions, 1–3 feet thick next the limestone sloping walls, containing the angular fragments of "plate-rock." This portion of the deposit alone is considered of commercial importance. In working the mine, the matrix, however rich in phosphoric acid, is washed away.

(4) To the opening at the bottom, between the base of the pinnacles, connected with a subterranean drainage. This is not universal in all the pits, but so general, as in those at Anthony, that it may be considered as a phenomenon of all the deposits in this elevated region. When the elevation is small, as at Welshton, no opening to take off the leachings has, as yet, been observed. However, mining there has progressed but little.

(5) The "pinnacles" are evidently upward projections of the bed-rock Eocene limestone of the country. They are seen in these excavations (and in all of them except one great pit of the Pen. Phos. Co. northward of Sparr) without definite order or arrangement and of all sizes and shapes. The walls are often sloping as in the figure, often vertical and eroded into hollows and into deep round wells or pot-holes, washed out by the waves of a restless sea.

It would be tedious to enumerate all the mines in this region, and comment on the peculiarities of each, and it would serve no general purpose. Suffice it to say, the variations are principally in the phenomena of erosion, both before and subsequent to the deposition of the phosphates. Of these the general facts are about the same.

Reference has been made to the occurrence of fossils within the workable deposits. There are none, with only one excep-

tion as yet observed—at Belleview on the Florida Central and Peninsula railroad, 12 miles south of Ocala. The remains are chalcedonized oyster shells. As related by the manager of the mine they are associated with the "plate-rock" next the shoulders of Eocene limestone. As observed by the writer in an abandoned pit, where it was said they had been numerous, the shells of *Ostrea Virginiana* were still adhering to the rock, evidently undisturbed since the day they attached themselves, and grew there.

B. Genesis of the Plate-Rock Deposits.

The problems presented by the foregoing facts are: (*a*) To account for compact phosphate; (*b*) To account for the "soft-phosphate" phase; (*c*) To account for the presence therein of "*plate-rock*."

Peninsular Florida first appeared above water in early Miocene times, in the form of numerous small islands of Eocene limestone, stretched along what would later be the Gulf coast —corresponding in position to parts of the present counties— Suwanee, Columbia, Lafayette, Levy, Hernando, Citrus, Pasco, Sumter, and the western parts of Marion and Allachua. Twenty miles eastward of this main line facing the Gulf, was this smaller cluster of islets we have under consideration, then braving the Atlantic. Denudation of these islands by the sea imparted to them at many points the water-worn low bluffs with pinnacles, such as are visible on any part of the present coast composed of rocks like these. Notably may be instanced, St. Mark's Bay, and Deadman's Bay, of the Gulf side. Upon shores of this nature were laid down the deposits described in the foregoing pages.

The varieties of this class of phosphates in Marion County alone, comprise in mining language "hard rock," "laminated-rock," "plate-rock" and "soft-phosphate."

The explanation offered herewith of the *genesis* of these phosphates, is based upon the hypothesis of the original deposition of *guano*.

In a rainless region the deposits would have remained in form similar to those of the Chincha islands. In the present case in a region of much rain and great moisture, the guano beds became converted into the phosphates here encountered. The arrangement of land and sea in the Miocene age rendered the deposition of immense deposits of *guano* quite possible. Only upon such secure island homes, away from the predatory animals of the continent, could the sea-birds have successfully maintained their breeding grounds. The waters of such an archipelago at that age teemed with life, which with the rich vegetation of warm shallow seas afforded ample food.

Having the material deposited, adequate to furnishing a supply of phosphoric acid, the process of change to the present forms followed as a natural consequence, from the attendant circumstances in due course of *law*. The guano beds after the leaching out of their carbonates and other soluble materials, became very compact, yet not entirely impervious to water. It is probable that some waste of material by solution is continued in degree to the present day.

Cavities are found in the most compact beds of the "hardest rock." Small cavities in close contiguity became finally separated by mere plates, and in this condition are called "*laminated-rock*."

By further disintegration such laminated rock is broken up into fragments greater or less, and is then "plate-rock"—such as is found mixed up with more finely comminuted material in the deposits of Anthony and Sparr and Fairview clinging to the walls of the pinnacles of Eocene limestone.

Still further progress of the disintegrating process results in the masses of "soft-phosphate"—the impurity of the final material depending in part upon the amount of clay originally contained in the immense deposits of the original rock, and partly upon the amount of extraneous matter washed in.

That the fragments of "plate-rock" should cling to the walls of the pits is the natural result of drainage being more energetic in the center of the hopper than at the sides; at the same time the middle portions become dissolved or reduced more quickly and more completely than the exterior.

ART. LXI.—*On Electrical Oscillations of Low Frequency and their Resonance;* by M. I. PUPIN, Ph.D., Columbia College.

PART II.

[Continued from page 429.]

V. *Electrical Resonance in mutually inductive circuits.*

a. The impressed Electromotive force is a simple harmonic.—The primary circuit consists of a coil which is in series with a condenser and an alternating current machine which generates the impressed e. m. f. $E \sin pt$. The secondary circuit consists of a coil joined in series to a condenser. The secondary coil consists of several parts, some or all of which are under the inductive action of the primary circuit. The

electrostatic capacity of the coils is small in comparison to the capacity of the terminal condensers. *Foucault currents and hysteresis losses are supposed to be negligibly small.* The symbolical expressions of the generalized form of Ohm's law will be, in the well-known notation of Maxwell:—

$$\left.\begin{aligned} L\frac{dx}{dt} + M\frac{dy}{dt} + Rx + P_1 &= E\sin pt \\ N\frac{dy}{dt} + M\frac{dx}{dt} + Sy + P_2 &= 0 \ldots \end{aligned}\right\} \quad (9)$$

Remembering that a circuit consisting of coils whose coefficient of self-induction is L and a condenser of capacity C in series with these coils may be treated analytically like a closed circuit with no capacity but having a coefficient of self-induction equal to $\frac{1}{p^2C}-L$,* where p is the pulsation of the impressed e. m. f., it is clear that the integrals of (9) are obtained from the well-known integrals of the ideal transformer † by the following substitutions:—

$$L_1 = \frac{1}{p^2C_1} - L \qquad L' = L_1 - \frac{p^2M^2N_1}{p^2N_1^2+S^2}$$

$$N_1 = \frac{1}{p^2C_2} - N \qquad R' = R + \frac{p^2M^2S}{p^2N_1^2+S^2}.$$

When the circuits are in resonance to the impressed e. m. f. then both L_1 and N_1 are zero. Hence

$$\left.\begin{aligned} x &= \frac{SE}{p^2M^2+RS}\sin pt \ldots \\ y &= \frac{pME}{p^2M^2+RS}\cos pt \ldots \end{aligned}\right\} \quad (10)$$

The corresponding amplitudes of the condenser potential differences are given by

$$\left.\begin{aligned} P_1' &= pL\,\frac{SE}{p^2M^2+RS} \ldots \\ P_2' &= pN\,\frac{pME}{p^2M^2+RS} \ldots \end{aligned}\right\} \quad (11)$$

Let W_1 = work done in the primary circuit.
W_2 = heat developed in primary circuit.

* See this Journal, May 1893, p. 425, footnote.

† Fleming: Alternate Current Transformer, vol. 1, p. 154.
Pupin: Practical Aspects of the Alternating Current Theory, Transactions of the American Institute of Electrical Engineers, Vol. vii, May 1890.

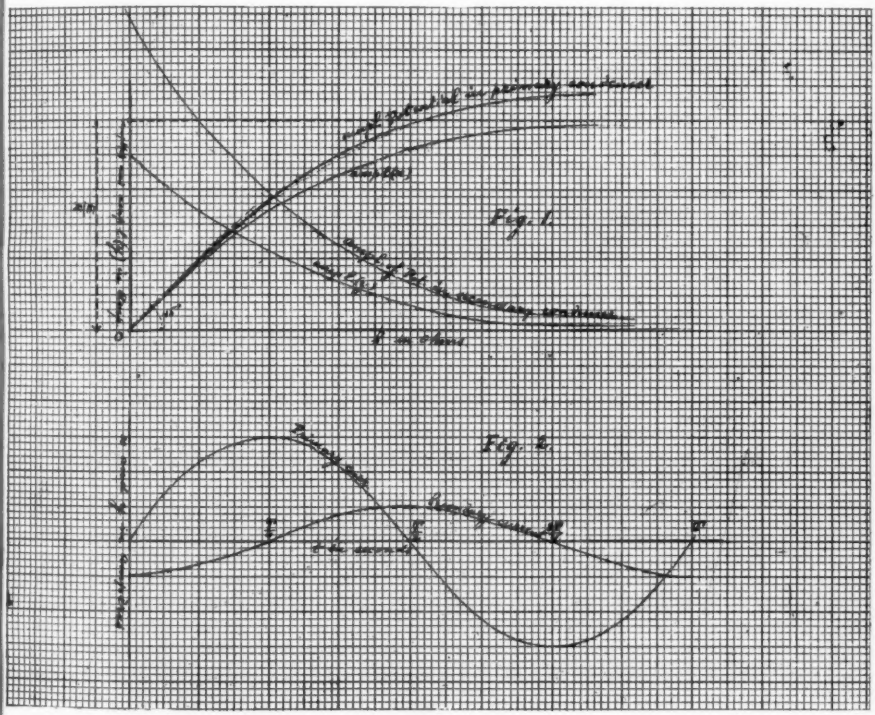
Hence $W_1 - W_2 =$ work transferred from the primary to the secondary circuit.

$$\frac{W_1 - W_2}{W_1} = \varepsilon = \text{ratio of transference.}$$

A simple calculation gives

$$\varepsilon = \frac{p^2M^2}{p^2M^2 + RS}$$

The higher the frequency the higher will be the ratio of transference other things being equal. The curves expressing



the relation between the resistance in the secondary circuit as abscissæ and the amplitudes of primary and secondary currents and potential differences in primary and secondary condenser

as ordinates are given in Fig. 1. The current curves are given in Fig. 2. (I am very sorry that these diagrams have come out very indistinct in the reproduction.)

With small resistance in the secondary the efficiency is high but the output is very low, and vice versa, when the resistance in the secondary is large then the primary current is large but the efficiency is low.

With ordinary transformers we have just the opposite relations, namely, the lower the resistance in the secondary the larger is the current in the primary. Here, however, owing to the fact that the counter electromotive force in the primary produced by the variation of the secondary current differs by half a period in phase from the primary impressed e. m. f., it is evident that the larger the secondary current the smaller is the effective e. m. f. in the primary circuit and hence the smaller is the current.

Let E_c = counter electromotive force in the primary due to variation of the secondary current.

Then $$E_c = M\frac{dy}{dt} = -\frac{p^2M^2E}{p^2M^2+RS}\sin pt.$$

Hence effective e. m. f. in the primary

$$= E\sin pt - E_c$$
$$= \frac{RSE}{p^2M^2+RS}\sin pt.$$

When $S = 0$ then the primary current would be equal to zero but the secondary would have its highest value

$$= \frac{E}{pM}.$$

These few remarks seem sufficient to clear up the rather surprising relations which the curves in fig. 1 illustrate.

When the frequency is very high, say 10^4 periods per second, then as long as S does not increase beyond the value at which RS is comparable to p^2M^2 so long will

$$\left.\begin{aligned} x &= \frac{SE}{p^2M^2}\sin pt \ldots . \\ y &= \frac{E}{pM}\cos pt \ldots . \\ P_1' &= pL\frac{SE}{p^2M^2} \ldots . \\ P_2' &= pN\frac{E}{pM} \ldots . \end{aligned}\right\} \quad (10^a)$$

Denoting the limiting values of these quantities (for $S = \infty$) by brackets we shall have

$$\left.\begin{aligned} (x) &= \frac{E}{R}\sin pt \\ (y) &= 0 \\ (P_1') &= \frac{pL}{R}E \\ (P_2') &= 0 \end{aligned}\right\} \quad (11^a)$$

as it should be.

The curves given in fig. 1, fig. 2 hold true in this case also but with this characteristic difference that for all variations of S between 0 and a considerably large limit (especially if R is very small, as in the case of Tesla's high frequency circuits) the secondary current and secondary potential are practically constant. The higher the frequency the larger is this limit.

More than ordinary interest is attached to the relations given in (10^a), because they give an approximately correct account of the electrical flow in the secondary circuit of an induction coil when the primary is excited by a Tesla high frequency alternator, the primary coil of the induction transformer, a condenser of suitable capacity and the alternator being connected in series. It must be observed, however, that since in general the induction coil which Mr. Tesla employs in his experiments does not differ essentially from the ordinary induction coil except that practically no iron is used—it is evident that the secondary coil has distributed capacity which if not necessarily as large as the capacity which would bring this circuit in resonance to the impressed e. m. f. at Mr. Tesla's high frequencies is certainly far from being negligibly small in comparison to it. For this reason equations (10^a) do not give the exact mathematical relations of Mr. Tesla's circuits. It is evident, however, that the values which these equations assign to the secondary current and secondary potential are the largest values which Mr. Tesla's circuits can possibly yield.

I do not find a single discrepancy between the theory just given and Mr. Tesla's experimental results. A full discussion of these results from the standpoint of this theory would lead me far beyond the limits of this paper. A few brief observations relative to the agreement between theory and Mr. Tesla's experiments* seem desirable:

a. On account of the considerable internal capacity of Mr. Tesla's induction coils there is a critical speed of the generator at which a large secondary coil by its own internal capacity will be in resonance to the impressed e. m. f. If it is desira-

* See Mr. Nikola Tesla's lecture in the N. Y. Electrical World, vol. xviii, July 11, 1891, p. 20.

ble to add capacity to the terminals of the secondary coil then the speed of the alternator must be below this critical point.

b. By diminishing the speed it is possible to increase the terminal capacity without diminishing perceptibly the secondary voltage. Hence the secondary current will be thereby increased and therefore the physiological effect of a lower frequency Tesla current may be considerably more powerful than that of the higher frequency.

c. At very high frequencies, say 10^4 periods per second the Tesla current will in general be exceedingly small, considering that the impressed e. m. f. of his generator is about 140 volts only. Hence the physiological effect of these currents will also be small. (But I do not wish to be understood as denying that the rapidity of reversals in itself diminishes the physiological effect.)

d. Since the rise of potential will be the higher the smaller the dissipation of the work which the impressed e. m. f. does it is evident that dielectric hysteresis, in consequence of which the dielectrics are heated, will pull down considerably the secondary voltage. It is therefore desirable to employ liquid or solid dielectrics of small specific inductive capacity, since in these the heating due to dielectric hysteresis is smaller than in dielectrics of high inductive capacity.

e. It is evident that by a suitable diminution of the coefficient of mutual induction M within the limits within which $p^2 M^2$ is considerably larger than RS for the highest value of S at which the high frequency system is expected to run both the secondary current and the secondary e. m. f. can be increased very considerably. This could be done by dividing the secondary coil into two parts and allowing one part only (and that too probably the smaller part) to surround the primary coil, in which case the remaining part would be employed as additional inertia coil in the secondary circuit, this inertia coil performing the function of assisting the impressed e. m. f. to produce a high rise of potential in the secondary circuit. In one of his papers* Mr. Tesla mentions that, by removing partly the primary coil from the secondary, higher potentials can sometimes be produced, and the output of the secondary circuit very much increased. "*St. Elmo's Hot Fire*" is the name which Mr. Tesla gives to the powerful flame discharge obtained, by this arrangement of the two coils, from one of the secondary poles, when the other pole (the terminal of the secondary turns which are nearest to the primary coil) is connected either to the primary or to a body having considerable capacity. Mr. Tesla states that his object in arranging the

* See Mr. Tesla's article cited above, p. 23.

coils in the manner just described was for the purpose of avoiding the brush discharges between the primary and the secondary coils. He does not seem to have been aware at that time of the fact that by this method of arranging the two coils it is possible to obtain another and probably quite as important advantage, namely: to diminish the number of turns in the secondary coil very much and thus diminish its resistance, capacity and self-induction and all the evils connected therewith and therefore to increase the secondary terminal capacity and potential. In such an arrangement the relations of (10^a) are very nearly true and the nearer they are to the truth the higher will be the output and the efficiency of the high frequency system.

These few observations will suffice to point out that on the one hand the high frequency currents as developed by Mr. Tesla are resonant electrical oscillations, whose period is very long in comparison to the period of Herzian oscillations, and that on the other hand their mathematical theory is simply the theory of the ordinary low frequency resonance given in this and the preceding paper.

It is my pleasant duty to thank Mr. Tesla on this occasion for the favor which he conferred upon me by lending me his remarkable apparatus for a few days. My short experience with it has taught me many an instructive lesson for which I feel very grateful to Mr. Tesla.

Before describing some of my experiments on resonance in mutually inductive circuits with low frequency impressed e. m. f. it seems desirable to point out the relations in mutually inductive circuits when the primary circuit contains no condenser.

When an alternator containing iron in the armature is employed to generate the impressed e. m. f. then this method of arranging the circuits must be adopted in experiments on resonance, especially when the frequency is over 100 periods per second. The reason for this will be apparent further below. For this arrangement of the circuits we shall have when resonance is established in the secondary circuit

$$x = \frac{ES}{\sqrt{p^2L^2S^2+(p^2M^2+RS)^2}} \sin(pt-\varphi) \qquad (13)$$

$$y = \frac{pME}{\sqrt{p^2L^2S^2+(p^2M^2+RS)^2}} \sin(pt-\psi) \qquad (14)$$

$$\tan\varphi = -\cot\psi = \frac{pLS}{p^2M^2+RS}.$$

Hence

$$\varphi = \frac{\pi}{2} + \psi.$$

Let P_2 = amplitude of the potential difference in the secondary condenser, then

$$P_2 = pN \frac{pME}{\sqrt{p^2L^2S^2 + (p^2M^2 + RS)^2}}. \qquad (15)$$

When R^2 is small in comparison to p^2L^2 and p^4M^4 is small in comparison to $p^2L^2S^2$ then

$$P_2 = pN \frac{M}{L} \frac{E}{S} \qquad (16)$$

which is the same in form as relation (8) in the preceding paper *

These relations differ very little from those in (10) and (11); hence curves fig. 1 and fig. 2 will apply to this case also.

The theory of low frequency resonance in mutually inductive circuits when the impressed e. m. f. is a complex harmonic is of no importance in connection with experiments in which the impressed electromotive force is generated by an ordinary alternating current machine, because the upper harmonics, as will be seen presently, are almost entirely absent then. When the alternating current is produced by transforming an interrupted current, then, since in this case the currents employed are small and therefore the iron cores but slightly magnetized, the harmonics are incomparably more persistent.

I prefer to discuss first those experiments in which circuits with iron cores subject to considerable magnetizations are employed, and where a marked difference exists between theory and experiment because the behavior of iron is so peculiar then and so strongly brought out by resonant circuits that these experiments appeared to me of much greater importance than the experiments with circuits without iron which circuits, having no hysteresis losses, bear more directly upon the theory of what may be called Ideal Low Frequency Resonance.

Description of Experiments.

The alternator was a 1 H-P machine consisting of a Gramme ring armature with 16 poles, such as is used in the Crocker-Wheeler motors. Its field magnet consisted of a cast iron ring with sixteen pole-projections. The field was separately excited. The armature rotated at the rate of about 2810 revolutions per minute, the e. m. f. had therefore about 375 periods per second. The amplitude of the impressed e. m. f. was about 600 Volts. The primary poles *cd* (fig. 3) of an induction coil were connected to the poles of the alternator. The primary of this coil consisted of 3000 turns of No. 20 B. & S. W. G. wire having a

* See this Journal, May, 1893, p. 426.

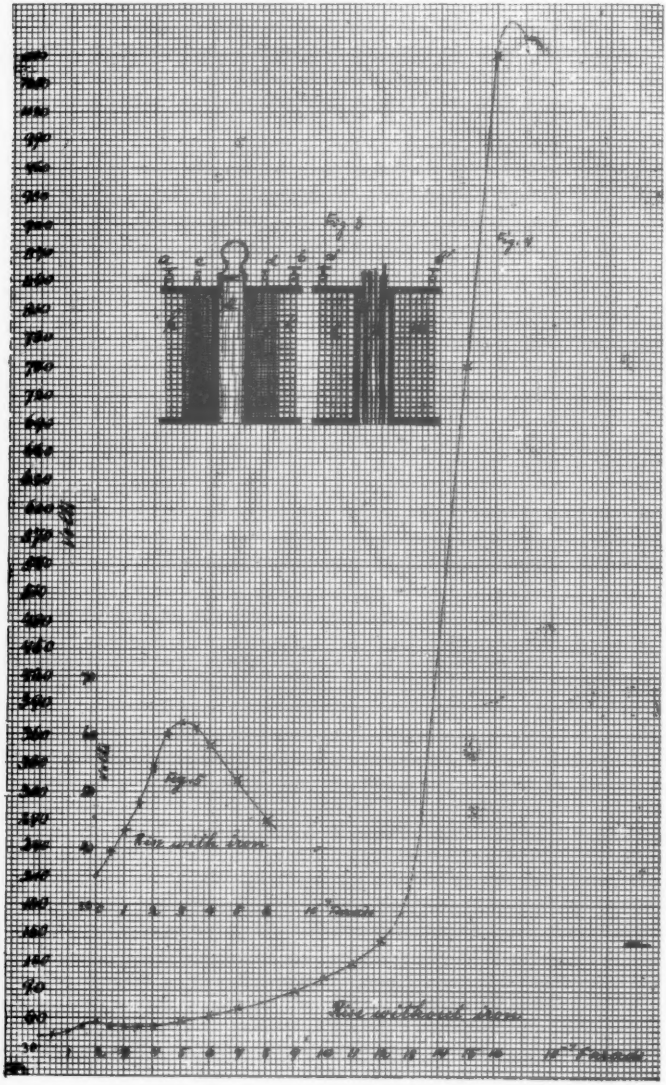
resistance of nearly 40 ohms. The secondary consisted of 120 turns No. 14 B. & S. W. G. wire. The iron core *e* was a cylinder of well packed fine iron wire. The diameter of this cylinder was 5^{cm} and its length 40^{cm}. High voltage was measured by a Thomson electrostatic voltmeter, small voltage by a Thomson multicellular voltmeter or a Weston alternating current voltmeter. It is, however, not advisable to use this last instrument in resonance work when the voltage exceeds 50 volts. An *inertia coil a' b'*, fig. 3 was connected in series with the secondary of the induction coil and also with an adjustable Marshall condenser of 1·9 microfarads, the smallest subdivision being 0·05 M.F. The inertia coil consisted of about 1000 turns of coarse copper wire, about No. 16, so that its resistance was only a few ohms. A removable iron wire bundle could be inserted into this coil, so as to study the effect of iron upon resonance.

The first series of experiments was done without iron in the inertia coil. The speed of the alternator was maintained at 2810 revolutions per minute or nearly 375 complete periods per second. The capacity was gradually varied from 0 to 1·6 microfarads when the maximum point of the voltage of the condenser was reached. The values are tabulated in table 1, curve fig. 4 (unfortunately very indistinct in the reproduction), was plotted from this table, by taking the capacities in 10^{-7} Farads for abscissæ and the corresponding difference of potential in volts in the condenser for ordinates.

TABLE I.

Condenser capacity in 10^{-7} Farads.	Corresponding value of the difference of potential of the condenser in volts.
·0	40·5
0·5	43·
1·0	46·
1·5	51·
2·0	56·5
2·5	53·
3·0	51·5
3·5	52·
4·0	53·
5·0	57·5
6·0	63·5
7·0	70·5
8·0	77·
9·0	89·
10·0	103·
11·0	118·
12·0	140·
15·0	750·
16·0	1090·

A simple consideration will show that the curve in fig. 4 is exactly the curve which theory demands; but, as I stated



before, *I prefer for the present to discuss those cases in which there is an apparently striking disagreement between theory and experiment.*

When the maximum point is reached then the slightest variation of the capacity one way or the other causes a very large variation in the potentials. The curve of potentials looks and behaves just like a sensitive flame. The maximum potential is at about 1·66 microfarads. There is however another maximum at about 0·18 microfarads which would correspond to the first upper harmonic. This second maximum has been determined with exceedingly great care, so that there is not the slightest doubt about its existence. From the shape of the curve one is led to infer that the form of the impressed e. m. f. is given by

$$E = a_1 \sin pt + a_3 \sin 3\,pt.$$

where the amplitude a_3 is exceedingly small. This was rather surprising, since, owing to the peculiar shape of the armature one would have expected a much stronger development of the upper harmonics.

Before I obtained the alternator just described my experiments on the rise of potential by resonance were all performed by means of alternating currents obtained from the interrupter described in my first paper.* In these experiments, an account of which will be given at some future time, the upper harmonics appear very strongly in curves corresponding to the curve in fig. 4. In fact, the crest corresponding to an upper harmonic can be made considerably higher than that corresponding to the fundamental. In the experiment with our large alternator giving about 100 periods per second, which experiment I described in my last paper† the upper harmonics seemed to be present in strong force although the armature of this alternator has no iron projections nor is the machine in any other respect as apt to generate a complex e. m. f. as the small machine described above. The consideration of the circumstance that since the small machine generated an e. m. f. of nearly four times the frequency of that generated by the large machine and that therefore in the case of the small machine the self-induction is much more effective in destroying upper harmonics did not seem to explain matters quite satisfactorily. There was evidently something going on in my circuits during those experiments† that I did not understand clearly.

* This Journal, April, 1893.

† This Journal. May, 1893, pp. 426, 427 and 429.

IV. *On the Effect of Iron upon Resonance and the Relation between this Effect and the Frequency.*

Experiment 1.—A few iron wires were then introduced into the inertia coil and the secondary circuit was tuned To my great surprise, I found that now the upper harmonic maximum had disappeared and the maximum rise had diminished quite perceptibly, although the self-induction of the inertia coil and therefore of the whole resonant circuit had been considerably increased. But I must mention here that the iron got so hot in a few seconds as to cause the fibre spool of the inertia coil to smoke where the wire touched it. There was a serious discrepancy between experiment and formula (15). To bring out this discrepancy very strongly I placed all the iron wire into the inertia coil (about 500 wires, each 40^{cm} long and 1^{mm} in diameter). On tuning the circuit it was found that the maximum potential was reached at considerably smaller capacity and that the rise of potential was incomparably smaller than in the previous case. Table II gives the experimental data, the curve in fig. 5 was plotted from this table. The frequency was maintained nearly the same as in the previous experiment, namely 375 complete periods per second.

TABLE II.

Capacity in 10^{-7} Farads.	Difference of potential in the condenser in Volts.
·0	35·5
0·5	39·5
1·0	43·
1·5	48·
2·0	54·
2·5	60·
3·0	62·
3·5	61·
4·0	58·
5·0	52·
6·0	45·

In the experiment (described in my last paper) with our large alternator giving 100 periods per second I obtained with similar inertia coil and the same iron wire a rise from 60 to 900 volts. In this experiment with four times the frequency I expected to get nearly four times the rise and instead of that there was hardly any rise at all. I inferred, therefore, that the presence of iron in all probability diminishes at higher frequency the rise of potential due to resonance.

To investigate the relation between this damping of the iron and the frequency I substituted for the small alternator our

large alternator. The impressed e. m. f. was maintained constant and equal to about 1000 volts. The frequency was also maintained constant and equal to nearly 125 periods per second, hence just about $\frac{1}{8}$ of the frequency obtained by the small machine. The secondary was now tuned first when there was no iron wire core in the inertia coil. The condenser potential rose steadily until the maximum point was reached. There was no sign of an upper harmonic. This distressed me very much in view of the statement which I made in my last article concerning the presence of upper harmonics in the e. m. f. generated by this alternator. I had evidently blundered somewhere in my previous experiment with the large alternator. In my endeavors *to locate the blunder I discovered a very peculiar behavior of the iron when it is under the inductive action of a resonant circuit*, which behavior explained to me perfectly why in the experiment, which I described in my last paper,* there was a much higher rise of potential when the capacity was considerably increased without apparently increasing perceptibly the coefficient of self-induction.

Experiment 2.—I next placed the iron wire bundle into the inertia coil and found that the maximum rise was one half of the rise which was obtained without the iron, which showed that with the diminution of the frequency the damping effect of the iron upon resonance was much less. *If a high impressed e. m. f. is employed in the resonant circuit just described then the rise of potential can be made even higher with iron than without it at this frequency.* Increasing the capacity considerably and then raising the wire bundle until the maximum deflection in the Thomson voltmeter was obtained I found that only a slight displacement of the bundle was necessary to reach the point of resonance. The maximum voltage, or *the resonant rise*, was considerably higher. (It will be seen presently that under certain conditions the bundle can be lowered again without destroying resonance or diminishing the resonant rise and it was owing to this circumstance that in the experiment described in my last paper I believed that I was tuning the circuit to respond to an upper harmonic of the impressed e. m. f.)

Increasing the capacity again and then raising the iron wire bundle a little more the maximum potential was again increased until a point was reached at which the maximum rise of potential began to diminish when the capacity was increased and the iron wire bundle raised in order to establish resonance again. From this point on, which I shall call the

* This Journal, May, 1893, pp. 426, 427, 429.

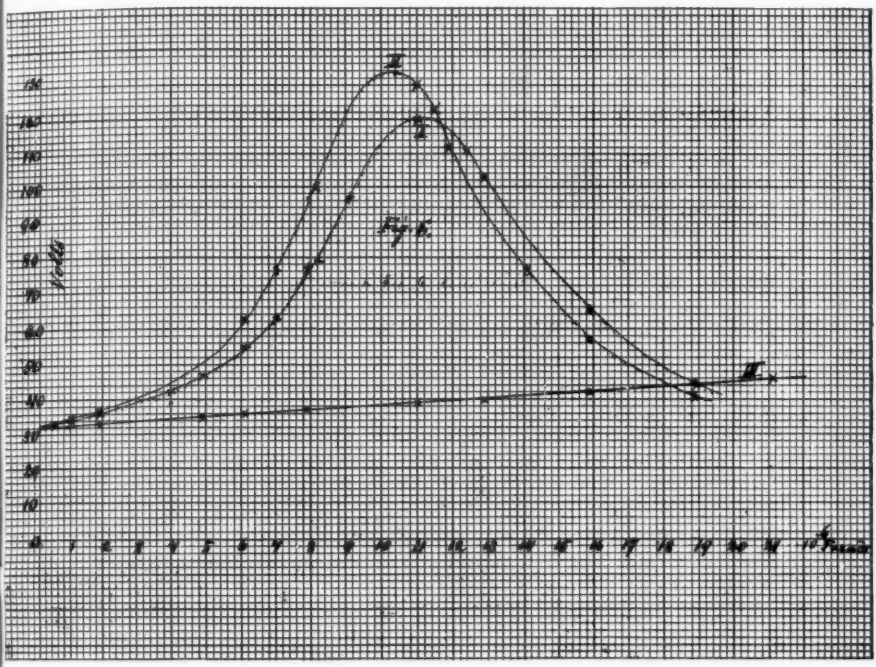
critical point, the rise of potential due to resonance fell off gradually until the iron wire bundle was entirely removed. *It is very instructive to observe that the position of the critical point changes perceptibly with the amplitude of the impressed e. m. force.*

It is evident, of course, that on account of hysteresis losses the rise of potential produced by resonance will be less than the theoretical value given by (15). And the first explanation which one will naturally offer for the above discrepancy between the theoretical and the actual value will be that as the quantity of iron wire in the interia coil is increased the increase of the coefficient of self-induction tends to increase the resonant rise but that on the other hand the increase of hysteresis losses due to the increased mass of iron tends to pull this rise down and that it is then simply a question of adjustment which one of the two tendencies will predominate. This explanation does not, however, cover the ground completely as will be found by the following experiments:

Experiment 3.—In order to experiment with lower frequencies, as they seemed to bring out this peculiar behavior of the iron more clearly, I substituted a one H. P. four-pole alternator for the large alternator. The speed was such as to give the impressed e. m. f. a frequency of 50 periods per second.

TABLE III.

Part A.		Part B.		Part C.	
Capacity in 10^{-6} Farads.	Voltage of the condenser.	Capacity in 10^{-6} Farads.	Voltage of the condenser.	Capacity in 10^{-6} Farads.	Voltage of the condenser.
0·0	32·	0·0	32·	0·0	32·
0·5	32·5	0·5	33·5	1·9	32·5
1·0	34·	1·0	34·5	4·9	35·
1·9	36·	1·9	37·	6·1	36·
4·1	39·	4·1	42·	7·9	37·
4·9	47·	4·9	52·	11·0	38·
6·1	51·	6·1	62·5	12·9	39·5
7·0	62·5	7·0	77·	15·9	42·
7·9	77·5	7·9	97·	18·9	44·
8·2	79·	8·2	100·	21·1	46·
9·1	97·	11·0	130·		
11·0	120·	11·5	122·5		
12·4	111·	11·9	112·		
12·9	103·	13·9	94·		
15·9	65·	14·1	77·		
18·9	45·	15·9	57·		
		18·9	41·		



One-half of the bundle of the iron wire was placed into the inertia coil and the circuit tuned. Table III, Part A, gives the data from which curve I, fig. 6, was plotted. Next all the wire was placed into the inertia coil and the circuit tuned. Table III, Part B, gives the data from which curve II, fig. 6, was plotted. Finally the circuit was tuned without any iron and from the data of Part C, Table III, curve III, fig. 6 was plotted.

From the curves I and II it is evident that the doubling of the mass of iron produced very little change in the values of the capacity and self-induction which established resonance between the circuit and the impressed e. m. f., and yet although the losses due to magnetic hysteresis were more than doubled (since the magnetizing current was a little larger with double the mass of iron in the inertia coil), yet the rise of potential due to resonance was increased. This experiment seemed to me to indicate that hysteresis and Foucault current losses do not explain quite fully the discrepancy between the theoretical and the experimental values of the rise of potential

due to resonance. Thinking that perhaps the development of Foucault currents in the rather coarse iron wire or that the mechanical vibrations of the wire may in some way or another modify the period of the circuit and the self-induction of the coil, I endeavored to devise some simple experiments which would test the hypothesis just mentioned.

Experiment 4.—About 19 microfarads were plugged in the condenser and then the iron wire was gradually introduced into the inertia coil and the rise of potential was observed closely. The potential went up continually until a maximum of about 100 volts was reached. From this point on the electrometer needle remained stationary although I kept on adding more and more iron wire, one wire at a time. Suddenly the addition of another wire caused the electrometer needle to drop down considerably below the midway point between zero and the maximum point. I tried then to bring it back by removing the iron wires slowly one at a time from the inertia coil and found that I had to remove a considerable number of wires (about one fourth of the total number which was about 300 wires) before the electrometer index began to move up rapidly toward the maximum point previously obtained. The wires were now gradually replaced into the coil and the same phenomenon observed as before. The experiment was repeated over and over with invariably the same result.

Experiment 5.—After the collapse of resonance (as described in the last experiment) by the addition of the last fatal wire, as it were the last straw that broke the camel's back, resonance, indicated by the large rise of potential and the singing of the iron wire, was established again by gradually lifting the whole bundle until the electrometer indicated the highest point. Then the bundle was lowered again very gently until it was entirely in the coil again. The electrometer needle would then remain stationary, apparently for an indefinite time. But the mere approach of an iron wire toward the bundle would upset the resonance suddenly and cause the electrometer needle to drop way down. That this approach of the single iron wire did not disturb resonance by the increase of the coefficient of self-induction was proved by the circumstance that if this iron wire was introduced into the coil and then the whole bundle raised until resonance was established and then slowly lowered again the maximum potential previously obtained was reached again and maintained apparently indefinitely although the iron wire bundle contained now that wire also by whose mere approach resonance was upset before. In fact it is possible to increase in this way, the number of iron wires in the bundle by four or five wires without changing perceptibly anything in the resonant effect, whereas the mere approach of a single

wire from outside was sufficient to upset it entirely. In the course of these experiments it was observed that a gentle handling of the iron wire produced much more sensitive instability in the resonance. I suspected therefore, that mechanical vibrations of the wire might have something to do with the phenomena observed, and although I have been unable as yet to determine exactly to what extent these vibrations do influence the effect of iron on the resonance yet I feel that this effect is to a considerable extent due to molecular action of the iron. The following two experiments will, I venture to suggest, throw some light upon this point.

Experiment 6.—A sensitive resonance was obtained by placing a sufficiently large number of iron wires into the inertia coil until the addition of another wire caused a collapse. After the collapse the wire bundle was gently raised and then lowered again, 19 microfarads being plugged in the condenser. Now the capacity was varied by removing carefully one plug after another from the condenser. The capacity could thus be diminished fully 6 per cent without anything like a corresponding change in the resonant rise of potential. But a critical point in the variation of the capacity is then reached, after which the slightest change in the capacity will cause the resonant rise of potential to collapse suddenly, after which collapse the plugging in of the condenser plugs did not restore resonance. To bring resonance back again it was necessary to raise and lower again the wire bundle in the manner described above. *If however the capacity was varied by even less than* 1 *per cent, but in such a way as to allow a bright, snapping spark to take place when the condenser plug was removed, then the spark had almost invariably the effect of causing a collapse of resonance.*

Experiment 7.—All the preceding experiments were now repeated with the iron wire tied very tightly together and when the whole bundle was introduced into the inertia coil it was pressed tightly against the table so as to prevent mechanical vibrations as much as possible, but the phenomena described above appeared again. I observed however that the sensitiveness of the instability of the resonant flow was not quite as great as when the iron wires in the inertia were standing loosely.

All these phenomena are observable at high frequencies also but they are not marked as strongly as at low frequencies.

While working with weak alternating currents obtained by my electrodynamic interruptor, this peculiar behavior of iron was never observed by me, probably because in these circuits the magnetizations are so weak that iron is capable to follow every impulse of the magnetomotive force. Hence the persist-

ance of the upper harmonics in resonant circuits through which weak currents flow, and their entire absence from resonant circuits traversed by strong currents.

I expect to follow up this subject more closely and I do not know of any method by which it could be studied with greater ease and accuracy than by the method of resonant rise of potential. *The circumstance that low frequency resonance offers so delicate a method for the study of electromagnetic phenomena such as I just described seems to me to make the subject of slow frequency resonance even more important than the fact that by it rise of potential and weeding out of harmonics can be produced.*

Before closing this paper I must thank my pupil Mr. M. C. Canfield, postgraduate student in Electrical Engineering, for the very efficient way in which he has aided me in these experiments.

Electrical Engineering Laboratory, School of Mines,
Columbia College, New York, May 8th, 1893.

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *On the Loss of Energy due to Chemical Union.*—In order to measure the loss of energy due to a given chemical action, Gore has proposed to determine the electromotive force between a plate of platinum and a plate of some other metal (usually aluminum, tin, cadmium, zinc or magnesium) immersed first in the two given solutions separately and then in the two mixed together. Thus for example he takes a known quantity of an acid dissolved in a known mass of water and measures the electromotive force A developed by a small platinum-aluminum couple immersed in the solution. He then takes a quantity of a base chemically equivalent to this, dissolved in the same mass of water, and measures the electromotive force B developed by the same couple. Finally he determines in the same way the electromotive force C in a solution containing the equivalent quantity of the salt resulting from the combination of the acid and base already used. Multiplying then the equivalent mass of the acid into its electromotive force A, and that of the base into its electromotive force B, adding these together and dividing the sum of the products by the sums of the equivalents, he obtains a value D. Subtracting C from D and multiplying by 100 / D, the product represents the loss or gain of electromotive force in percentages; and this the author regards as expressing the relative loss or gain of molecular energy which has taken place upon the union of the acid and the base. In the paper the results of numerous experi-

ments made with substances of various classes, are given in the form of tables. They show that when an acid and a base neutralize each other an increase of electromotive force occurs in almost all cases; a similar increase taking place in eighty per cent of the cases even when the acid is neutralized by a carbonate. When saline solutions or acid solutions are mixed with each other very little change of electromotive force is noticed; though considerable changes are produced when saline solutions are mixed with acids. The above experiments were made with dilute solutions, one gram-equivalent of the substance being dissolved in 100 gram-molecules of water.—*Phil. Mag.*, V, xxxiii, 28, 1892. G. F. B.

2. *On the Preparation of Acetylene.*—A convenient method for the preparation of acetylene from inorganic materials has been described by MAQUONNE. Barium carbide is first prepared by mixing 20 grams of precipitated barium carbonate with 10·5 grams of powdered magnesium and 4 grams of retort carbon, previously heated in a platinum crucible; this mixture being placed in an iron bottle of about 700 c. c. capacity, to the neck of which is attached an iron tube 2 cm. in diameter and 30 cm. long. On heating the bottle to redness, an energetic reaction ensues, sparks being projected from the tube. When this ceases the tube is closed and the bottle is rapidly cooled. The product is a mixture of magnesium oxide containing about 38 per cent of barium carbide, with a trace of cyanide and some carbon. It is a light, porous, friable, amorphous mass, gray in color, permanent in dry air and not attacked in the cold by chlorine or hydrogen chloride. Acid oxides or chlorides, even phosphoric chloride do not act on it at 100°; but at a red heat it burns in air with vivid incandescence; as it also does in chlorine, vapor of sulphur and hydrogen chloride. When treated with water, or alcohol, or as a rule with any compound containing hydroxyl, at the ordinary temperature, barium carbide yields acetylene. If water be allowed to fall upon the carbide drop by drop, a regular current of acetylene is obtained containing two or three per cent of hydrogen and no appreciable trace of any other hydrocarbon, the yield being about two thirds of that calculated from the mass of magnesium employed. On passing the acetylene through a long glass tube heated to a dull redness, the author has obtained several grams of synthetic benzone in one day.—*C. R.*, cxv, 558; *J. Chem. Soc.*, lxiv, ii, 62, Feb. 1893. G. F. B.

3. *On a New Alcohol of the Fatty Series.*—The trunks of the tree *Alnus nicana*, growing in Finland, were observed to be covered in the summer time, with a white powder. This powder, which was found to be a secretion from certain glands on the back of the plant louse *Pyslla alni* living upon the tree, has been examined by SUNDWIK. The dry insect was collected in quantity, exhausted first with hot ether and then repeatedly with hot chloroform. The latter solution on cooling deposited silky needles having the properties of an alcohol and the composition $C_{33}H_{65}(OH)$. From its origin the author calls it psyllostearyl alcohol. It fuses

at 95°–96°, is easily soluble in chloroform and acetic oxide, sparingly in absolute alcohol, insoluble in ether. It gives no reaction for cholesterin and is not altered by acetic oxide or caustic alkali even on fusion. By heating with 45 per cent hydrogen bromide to 210° or 220°, it gives a bromide melting at 85°–87°, containing 14·5 per cent bromine. On treatment with potassium hydroxide all the bromine is removed.—*Zeitschr. physiol. Chem.*, xvii, 425; *Ber. Berl. Chem. Ges.* (Ref.), xxvi, 100, Feb. 1893. G. F. B.

4. *On the Identity of Caffeine and Theine.*—Although caffeine was first isolated from coffee in 1821 and theine from tea in 1827, their chemical identity has only now been established by the researches of DUNSTAN and SHEPHEARD. Although this identity seems never to have been questioned on chemical grounds, yet the physiological action of the two seemed to indicate an isomerism between caffeine and theine. The caffeine used in the investigation was prepared from the unroasted coffee berries, by extracting with boiling water, evaporating to a small bulk, mixing with lime, drying on the water bath, and treating with boiling alcohol. After removing the alcohol, the residue was dissolved in one per cent sulphuric acid, filtered, treated with ammonia, and the caffeine extracted with chloroform. Repeated recrystallization from water gave silky needles fusing constantly at 234·5°. The theine was prepared similarly from tea. It crystallized also in silky needles fusing at 234·5°. To confirm this supposition of their identity, both bases were converted into aurochlorides and into mercurochlorides. When caffeine hydrochloride and auric chloride are mixed together the aurochloride separates on cooling in orange needles. The two aurochlorides appeared identical, fused at 242·5° and 243°, lost at 100° 6·3 per cent of water, and the anhydrous salt fused at 248·5°. The mercuro-chlorides also appeared identical, the pure salt made from theine as well as that made from caffeine fusing at 246°. The authors conclude therefore that there is no chemical ground for supposing caffeine and theine to be structurally isomeric. Several new gold compounds of caffeine are described in the paper.—*J. Chem. Soc.*, lxiii, 195, February, 1893. G. F. B.

5. *Lehrbuch der allgemeinen Chemie;* von W. OSTWALD. IIte Auflage. Band I, 1163 pp.; Band II, erster Teil, 1104 pp. Leipzig, 1891–93. (W. Engelmann). The appearance at this time of the first two volumes of the new edition of Ostwald's famous *Lehrbuch* will no little enhance the rapidly growing interest which has been aroused by the wonderful development of all phases of the theory of chemical processes during the past decade. Ostwald's style is historical and his treatment exhaustive. The first volume takes up *Stoechiometrie* and includes the modern Theory of Solutions.

An unusual measure of interest is excited by the succeeding volume, on Chemical Energy, for the reason that here for the first time in the history of chemical theory the General Doctrine of Energy is exhaustively developed and applied. Thermochemistry, Electro-

chemistry and Photochemistry are regarded as treating the transformations between chemical energy on the one hand, and heat, electricity and radiant energy on the other. The substantiality of energy, its forms, its capacity and intensity factors and the laws of its transformations are brought out and emphasized, the significance of the intensity factor of chemical energy, the chemical potential, in the theory of chemical equilibrium is made apparent, the history of the energy doctrine is outlined.

The "Thermochemistry" is very complete, both in theory and data. The "Electrochemistry" is a brilliant piece of work. The historical development, from Grotthus to the free-ion theory, from Hittorf and Kohlrausch to Arrhenius and Ostwald, is most interesting, and it is followed by a complete discussion of the magnificent results in the theory of concentration currents and of the galvanic cell, the whole treated from one point of view, as necessary deductions from the energy laws. Many new conclusions are drawn and confirmed by experiment; the whole reads like an original paper and is inspiring in the extreme. The volume is concluded by a similar presentation of the facts and theories of Photochemistry. J. E. T.

6. *Simplification of Tesla's Experiments.*—The glowing of a vacuum tube with or without electrodes can be shown by bringing it in contact with one pole of a Ruhmkorff coil or in the neighborhood of an insulated metallic plate which is connected with one pole of the Ruhmkorff. If one pole of a small Ruhmkorff is touched by the hand and a vacuum tube held in the other hand, it can be made to glow.—*Beiblätter zu den Annalen der Physik und Chemie*, p. 237. J. T.

7. *Loss of Electric Charges in diffuse light and in darkness.*—Edouard Branly finds that a disc of polished aluminum, experimented on a few days after being polished, slowly loses its charge. If the disc has been freshly polished the loss is rapid, even in diffuse light, and is only slightly diminished by surrounding it with orange light, thus showing that the loss is not due to any great extent to the refrangible rays of the spectrum.—*Comptes Rendus*, April, 1893. J. T.

8. *Influence of the character of metallic points on alternating discharges of Electricity between them.*—Wurtz states that iron terminals give small sparks. Copper and copper alloys give strong ones. An arc cannot be established between iron electrodes with a difference of potential of 1,000 volts. Steel, copper, phosphorus, bronze, aluminum bronze, tin and nickel also give no result. Zinc and also antimony resist a difference of potential of 1,000 volts. It is apparent that certain metals give off a metallic vapor in the electric arc which lessens the resistance of the arc. While other metals form an oxide which diminishes the arc by reason of its great resistance. The shorter this distance between electrodes of zinc and antimony up to one millimeter, the less permanent is the arc from an alternating current of 1,000 volts. If the air gap is increased to 5^{cm} the arc is more permanent.—*Lumière Electrique* 45, p. 79, 83, 1892. J. T.

9. *Registration of Magnetic variations.*—ESCHENHAGEN, at the magnetic observatory of Potsdam, employs a length of abscissæ equal to 20^{mm} per hour and obtains a fine curve by diaphragming the lens, determining exactly its chemical focus and by employing a very small mirror. The slit employed is $0{\cdot}25^{mm}$. The magnetic mirror is made in three parts or facets inclined to each other at an angle of 3°. It is enclosed in a bell jar in which the air is kept dry and free from sulphur vapor. The mirror gives three beams. During a strong disturbance just before the beam from the middle mirror leaves the drum, another point appears on the opposite side, which continues the record.—*Met. Zeitschr.; Nature*, April 6, 1893. J. T.

10. *Discussion of the Precision of Measurements with examples taken mainly from Physics and Electrical Engineering;* by SILAS W. HOLMAN. 176 pp. 8vo. New York, 1892. (John Wiley & Sons).—Professor Holman's work is of somewhat novel character, and will be of much service to students and workers in experimental physics, pure and applied. It discusses with thoroughness, and with numerous practical examples, the general subject of precision of measurements, first, direct, and second, indirect measurements. The author's wide experience has enabled him to select wisely the special kinds of measurements discussed, and it would be difficult to find in so convenient a form elsewhere the variety of material here brought together.

11. *Practical Physics: An Introductory Handbook for the Physical Laboratory;* by W. F. BARRETT and W. BROWN. Part I, Physical Processes and Measurements, the Properties of Matter. 284 pp. 12mo. London, 1892. (Percival & Co.).—This little volume presents in simple form, and with numerous examples worked out numerically, the introductory part of practical physics as needed by rather elementary students.

II. GEOLOGY AND NATURAL HISTORY.

1. *A new Geological Society.*—A Geological Society has recently been organized in Washington, D. C., for the presentation and discussion of topics of interest to geologists. The Constitution and standing rules were subscribed to by 109 founders at the first public meeting, March 8th, 1893. Its members are of two classes, active and corresponding. The annual dues of the first are $2, and of the second, $1. Meetings will be held on the second and generally also on the fourth Wednesday of each month from October to May, inclusive.

The journals and bulletins of the various societies appear to furnish sufficient opportunity for the publication of papers read before the Society, so that for the present the Society will not undertake to publish the papers presented. It will probably issue one bulletin each year containing the address of the retiring President and such other matter as the Council directs. All

publications, and if desired notices of the meetings also will be sent to corresponding as well as to active members.

The above circular has been issued by the Secretary, J. S. Diller.

2. *Zeitschrift für praktische Geologie: herausgegeben von* M. KRAHMANN.—This journal, the first number of which appeared with the beginning of the present year, is devoted to the practically useful and technical side of geology, and particularly to all in this line that relates to ores and ore deposits. It aims to give the latest information concerning new discoveries of deposits of the useful and precious metals, ores, coals, etc., of deep borings, mineral springs, concerning geological surveys, etc. It is to be issued monthly in large octavo form of 48 pp., is well printed and illustrated with maps, cuts, etc. The assistant editorial staff is a large one containing the names of many well known specialists both German and foreign. It is an excellent undertaking and will no doubt meet a well merited success. The publisher's address is Julius Springer, Monbijou-Platz 3, Berlin N.

L. V. P.

3. *Annals of British Geology*, 1891. A Digest of the books and papers published during the year, with occasional notes; by J. F. BLAKE. With six plates. pp. 402. London, 1892. (Dulau & Co.).—The second volume of the Annals of British Geology, for 1891, appears with admirable promptness. It gives abstracts, in some cases running to several pages, of upwards of six hundred papers upon British Geology, Paleontology, Mineralogy, Petrology and related subjects, with also papers on foreign geology published in Great Britain. It is a work which must be most useful to all engaged in labor in these fields, and there ought to be no question in regard to its present and future pecuniary support. Unfortunately it is suggested in the preface that the financial success of the series is not yet assured.

4. *Materialien zur Mineralogie Russlands*, von NIKOLAI VON KOKSCHAROW. pp. 97–137. Elfter Band. St. Petersburg, 1893. —This final part of the eleventh volume of the great Russian Mineralogy possesses a particular interest because issued so soon after the death of its distinguished and lamented author. The closing pages are devoted to an obituary notice giving a brief statement of his life and labors. Pages I to XI contain an index to the eleven volumes of this monumental work.

5. *Reports of the Missouri Botanical Garden.*—The princely endowment by which the late Henry Shaw of St. Louis established in the city of his adoption, a park, a botanic garden, and a school of botany, has already justified itself by its fruits. Under the administration of Professor William Trelease, the institution has accomplished much in the direction of improvement, and has encouraged research of a high order.

The fourth annual report of the Director is a worthy companion to those of previous years. It contains a list of plants collected by Mr. Albert S. Hitchcock, in a voyage to the Bahamas, together

with critical remarks on the subject of nomenclature. 953 species are enumerated, together with many varieties and some cultivated plants. The table of comparison shows that the Bahaman plants are of southern rather than of United States origin.

The following figures are taken from page 171 of the report.

Total in the Bahamas				380
Of which are found also in			Cuba	321
"	"	"	Mexico or Central Am.	197
"	"	"	South America	117
"	"	"	Virgin Islands	207
"	"	"	South Florida	129
"	"	"	Southern United States	68

Professor Trelease's contribution is entitled "Further studies of Yuccas and their pollination." The admirable work done by the late Dr. Engelmann and by Professor Riley on the cultivated specimens of *Yucca filamentosa* and *Yucca glauca* is now supplemented by field studies of these and other species, and the fascinating life-history of these plants and unconscious allies is approaching completion. Professor Trelease's accomplishments as an entomologist have stood him in good stead in the experimental investigation of Pronuba, so that his results taken in connection with those obtained by Professor Riley, and published in the third report of the Missouri Garden, have given a large number of the more essential facts connected with the plant and its dependent visitant. But the mystery of the coördinate evolution of the plant and the moth seems as deep as ever. It is to be hoped that this study which preserves so thoroughly the traditions of its founder's scientific adviser, George Engelmann, will not be abandoned until a satisfactory answer is given. The conjectures before us are fertile. The patient work on which they are based gives promise that before long, even more plausible conjectures may take their place. G. L. G.

Henry Eliason Seaton, A. M., Assistant Curator of the Gray Herbarium, Harvard University, died in Cambridge, after a short illness, on Sunday evening, April 30th. He entered the service of the University during the present academic year and by his courtesy and assiduity commended himself, at once, to all with whom he came in contact. His original investigations in regard to Mexican plants are of a high order and gave promise of great usefulness in systematic botany.

Mr. Seaton was born in Indianapolis, 15th April, 1869. He graduated in 1890 from Wabash College and became immediately the assistant of his botanical teacher, Professor John M. Coulter. In 1891, he accompanied his teacher, who had assumed the presidency of Indiana State University, to Bloomington, where he became instructor in Botany and Curator of the Herbarium. During that summer he visited southern Mexico and made large collections of plants. The elaboration of these and other Mexican species drew him to Cambridge, where his excel-

lent work attracted the attention of all connected with the Gray Herbarium. His untimely death is sincerely deplored by the botanical department of the University. G. L. G.

6. *Discoliths in clay beds;* by ARTHUR M. EDWARDS, M.D. (Communicated.)—Last winter the railroad officials were constructing a branch of the Pennsylvania Railroad across the meadows in Newark, N. J., to the north before crossing the Passaic River. They have been making the embankments of the sandy parts of the Amboy clays from near Woodbridge, N. J. I have examined the clay which came in the sand, which itself was light cream colored, almost white. There were five colored clays from white to dark gray. In the lighter colored kinds I find *Discoliths* and perhaps *Cyatholiths*. This is of importance for it makes the clay marine and also confirms the Cretaceous character of the deposit. The *Coccoliths* (which include *Discoliths* and *Cyatholiths*) exist now at the bottom of the ocean and occur in the chalk of the Cretaceous. They existed in the clays of Perth Amboy, N. J., and perhaps they will be found elsewhere.

III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *National Academy of Sciences.*—The following is a list of papers presented at the meeting held at Washington, April 18 to 20.

E. D. COPE: On the systematic relations of the Ophidia.

H. L. ABBOTT: Biographical memoir of General Montgomery C. Meigs.

M. C. LEA: On the nature of certain solutions, and on a new means of investigating them.

A. HYATT: The relations of allied branches of biological research to the study of the development of the individual, and the evolution of groups. The Endosiphonoidea (Endoceras, etc.), considered as a new order of Cephalopods. A new type of Fossil Cephalopod. Results of recent researches upon Fossil Cephalopods of the Carboniferous.

E. W. HILGARD: Biographical memoir of Julius Erasmus Hilgard.

A. S. PACKARD: Monograph of the Bombycine Moths of America, north of Mexico. Part I.—Notodontidæ.

G. W. HILL: Intermediary orbits.

RICHMOND MAYO-SMITH: The relations between the statistics of immigration and the census returns of the foreign-born population of the United States. Statistical data for the study of the assimilation of races and nationalities in the United States.

T. C. MENDENHALL: Telegraphic gravity determinations. Fundamental standards of length and mass.

H. S. CARHART: Comparison of latitude determinations at Waikiki. A one-volt standard cell.

R. H. CHITTENDEN: Peptonization in gastric digestion.

ALEXANDER GRAHAM BELL: Helen Kellar.

S. P. LANGLEY: On a potentiality of internal work in the wind. On a bolograph of the infra-red solar spectrum.

THEO. GILL: The classification of the gastropodous mollusks.

The Draper medal was presented to Professor H. C. Vogel.

2. *American Philosophical Society.*—The American Philosophical Society celebrated its 150th anniversary at Philadelphia during the week beginning Monday, May 22d. A reception, with

address of welcome by President Fraley was held on Monday evening, and morning sessions on the four following days with addresses and the reading of papers on various subjects. Many distinguished representatives of Foreign Societies announced their intention to be present.

3. *Hydrostatics and Elementary Hydrokinetics;* by GEORGE M. MINCHIN. 424 pp. Oxford, 1892. (*The Clarendon Press*, Macmillan & Co.).—The author professes to develop the mechanics of fluids only far enough to introduce a beginner to such writers as Besant, Lamb and Lord Rayleigh. Most students, however, will find all that they need in this volume. The work shows the same happy union of rigid analysis and clearness of statement found in *Uniplanar Kinematics.* We find in the preface two statements which seem to express the secret of Minchin's success as a writer of text books. "I am convinced that more than one-half of the efficiency of the teaching of any subject consists in the anticipation . . . . . of those difficulties which are certain to occur to the student, and which if left unnoticed [are] like uncaptured fortresses in the rear of an advancing army." Again—"The view that the fundamental notions of the differential calculus are a mystery . . . . which cannot be unveiled until great experience in mathematics has been attained has long seemed to be a most unfortunate fallacy." W. B.

4. *Elementary Mechanics of Solids and Fluids;* by A. L. SELBY. 299 pp. Oxford, 1893. (*The Clarendon Press*, Macmillan & Co.).—Mr. Selby is an excellent representative of the English Scientific Reformers. He shows an Euclidian regard for continuity of reasoning and his analysis follows the lines of the Calculus; though without using its symbols. Such a text book is elementary in form rather than spirit, and the student who undertakes it with the equipment of a little Geometry and Algebra, must read slowly enough to develop that mathematical insight which is the gift of nature to only the favored few. W. B.

5. *Poole Brothers' Celestial Planisphere and The Celestial Handbook.* [Compiled and edited by Jules A. Colas. pp. xiv, 110. Chicago, 1892 (Poole Bros., 316 Dearborn St.)—A popular work which will be found attractive by the class of readers for which it has been prepared and will tend to increase the general interest in the heavens and celestial phenomena. The planisphere is well constructed and convenient for use. A full commentary is given on each constellation comprising 140 figures, many of them original. Much of the material is collected from recent astronomical periodicals. Precise statement has sometimes been sacrificed to an effort to avoid technicality.

6. *Practical Astronomy;* by MICHIE and HARLOW. 218 pp. New York, 1893.—(John Wiley & Sons).—A full and well arranged guide for the observer and computer, which does not fill the place of Chauvenet's Astronomy, but will save its owner much turning of leaves in that book and the Nautical Almanac. The rules and forms for numerical computation are especially helpful.

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